Received by OSTI

JAN 07 1991

DOE/ER/13865--30

DE91 005717

PHYSICAL-CHEMICAL STUDIES OF TRANSURANIUM ELEMENTS

Progress Report

For the Period
April 1, 1988 - March 31, 1991

Joseph R. Peterson, Principal Investigator

Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600
(615) 974-3434
FAX: (615) 974-3454
Bitnet: JOEPETE@UTKVX

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PREPARED FOR

THE U. S. DEPARTMENT OF ENERGY

UNDER GRANT NO. DE-FG05-88ER13865

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DOE/ER/13865-030

PHYSICAL-CHEMICAL STUDIES OF TRANSURANIUM ELEMENTS

Abstract

Major advances in our continuing program to determine, interpret, and correlate the basic chemical and physical properties of the transuranium elements are summarized for the period April 1, 1988, through March 31, 1991. This program provides training for pre- and postdoctoral students in chemical research with the transuranium elements. New knowledge is being accumulated in the role of the 5*f* electrons in the bonding in actinide elements and compounds, the relationships of metallic structures to metallic valence and radius, the extent and magnitude of the actinide contraction, the magnetic, thermodynamic, spectroscopic, and crystallographic properties of these materials as related to general theories, the effect of self-irradiation on chemical and physical properties, the chemical and physical consequences of radioactive decay in the bulk-phase solid state, and in general, the range of validity of the actinide hypothesis.

TABLE OF CONTENTS

	Page
Introduction	1
Molar Enthalpies of Formation of $BaCmO_3$ and $BaCfO_3$	11
Luminescence, Absorbance, and Raman Studies of Europium Oxychloride at Various Pressures	21
Anti-Stokes Luminescence of Selected Actinide(III) Compounds	26

INTRODUCTION

The following constitutes the technical progress report of work performed under DOE contract number DE-AS05-76ER04447 (expired June 30, 1988) and DOE grant DE-FG05-88ER13865 during the period April 1, 1988, through March 31, 1991. The experimental work was carried out in the Transuranium Research Laboratory (TRL) of the Oak Ridge National Laboratory (ORNL), in the European Institute for Transuranium Elements (EITU) in Karlsruhe, Federal Republic of Germany (FRG), and in the National Synchrotron Light Source (NSLS) facility at the Brookhaven National Laboratory (BNL). Collaborative research efforts with members of the ORNL scientific staff have involved Drs. G. M. Begun, R. G. Haire, O. L. Keller, G. F. Payne, and J. P. Young. Research involving the structural analysis of selected lanthanide tribromides under pressure was performed via energy-dispersive X-ray diffraction analysis and via angle-dispersive X-ray diffraction using a position-sensitive detector in the EITU in collaboration with Dr. U. Benedict and Mr. S. Heathman. Attempts to identify a potentially new crystal structure of selected lanthanide tribromides under pressure via angle-dispersive X-ray diffraction analysis (performed at NSLS) were made by Dr. L. W. Finger of the Geophysical Laboratory, Carnegie Institution of Washington. Research collaboration with foreign scientists in the TRL included Dr. J. J. Fuger, EITU and University of Liege, Belgium. The names of these colleagues are given where appropriate in this report. Research results already submitted in either preprint or reprint form are not detailed again in this document, but they are to be considered an

integral part of it and are therefore listed by their DOE document numbers at the end of this introduction.

The following persons have received direct financial support under this contract/grant during the report period:

1. Joseph R. Peterson, Professor of Chemistry and Principal Investigator; Ph.D., University of California, Berkeley, 1967; from April 1988 through March 1991.

2. William R. Wilmarth, Postdoctoral Research Associate; Ph.D., University of Tennessee, Knoxville, 1988; from April 1988 through August 1988.

3. George M. Murray, Postdoctoral Research Associate; Ph.D., University of Tennessee, Knoxville, 1988; from September 1988 through May 1990.

4. Gang Chen, Postdoctoral Research Associate; Ph.D., Jilin University, Changchun (PRC), 1988; from October 1990 through March 1991.

5. Guillermo (Bill) D. Del Cul, Graduate Student Research Assistant; Ph.D., University of Tennessee, Knoxville, 1990; M.S., La Plata National University, Argentina, 1977; from April 1988 through September 1990.

6. Gary M. Finniss, Graduate Student Research Assistant; Ph.D. candidate, UT-Knoxville; B.S., West Virginia University, 1987; from June 1988 through July 1988.

7. Jean J. Fuger, Visiting Scientist/Professor of Chemistry; Scientific Coordinator, European Institute for Transuranium Elements, Karlsruhe, FRG; Ph.D., University of Liege, Belgium, 1959; August 1988, August 1989, and August 1990.

8. Robert V. Sarrio, Graduate Student Research Assistant; Ph.D. candidate, UT-Knoxville; B.S., Towson State University, 1985; from January 1989 through December 1989.

9. Jerry B. Burns, Graduate Student Research Assistant; Ph.D. candidate, UT-Knoxville; B.A., Carson Newman College, 1988; from May 1989 through March 1991.

10. G. Randy Hayes, Summer Research Assistant; B.S. candidate, UT Knoxville; from May 1990 through August 1990.

11. Norman E. Bores, Graduate Student Research Assistant; Ph.D. candidate, UT-Knoxville; B.S., University of Tennessee, Martin, 1990; from May 1990 through March 1991.

12. Nathan A. Stump, Graduate Student Research Assistant; Ph.D. candidate, UT-Knoxville; B.S., Huntington College, Indiana, 1987; from August 1990 through March 1991.

The following University of Tennessee, Knoxville personnel have collaborated with and/or received training from the principal investigator and his co-workers during the current report period but have not received direct financial support under this contract/grant:

1. Paul G. Huray, Professor of Physics; Ph.D., University of Tennessee, Knoxville, 1968; from April 1988 through July 1988.

2. Stanley E. Nave, Research Associate Professor of Physics; Ph.D., University of Tennessee, Knoxville, 1979; from April 1988 through September 1990.

3. Charles W. Duke, Science Alliance Summer Research Student; B.S. candidate, Presbyterian College, Clinton, South Carolina; from June 1988 through August 1988.

4. Norman E. Bores, Science Alliance Summer Research Student; B.S. candidate, University of Tennessee, Martin, 1990; from June 1989 through August 1989.

5. Mary C. Bowerman, ORNL/ORAU Summer Research Participant; B.A., Oklahoma City University, 1966; from June 1989 through August 1989.

6. C.-T. Phillip Chang, Postdoctoral Research Associate (with Stanley E. Nave); Ph.D., Iowa State University, Ames, 1989; from June 1989 through August 1990.

7. Vanna G. Faulstich, Undergraduate Student Participant in Research in Chemistry (Chemistry 400); B.S. candidate, UT-Knoxville; from September 1989 through December 1989.

8. G. Randy Hayes, Undergraduate Student Participant in Research in Chemistry (Chemistry 400); B.S. candidate, UT-Knoxville;from May 1990 through August 1990.

During the academic semesters of the current report period, the principal investigator devoted at least 5% of his effort to the research performed under this contract/grant. During the summer academic breaks he devoted 100% of his effort to the research performed under this contract/grant.

All documents produced since the last technical progress report (DOE/ER/04447-230) produced under the previous DOE contract DE-AS05-76ER04447 are listed here by DOE document number, title, author(s), location, and date of last submittal to DOE-Oak Ridge Operations or their present status.

1. (DOE/ER/04447-231) "Photoelectron Spectrometry of the Actinides from Ac to Es" by M. O. Krause, R. G. Haire, O. Keski-Rahkonen, and J. R. Peterson. Journal of Electron Spectroscopy and Related Phenomena 47, 215-226 (1988). Three reprints submitted September 16, 1988.

2. (DOE/ER/04447-232) "Absorption Spectrophotometric and X-Ray Diffraction Studies of the Trihalides of Promethium in the Solid State" by W. R. Wilmarth, R. G. Haire, J. P. Young, D. W. Ramey, and J. R. Peterson. Journal of the Less-Common Metals 141, 275-284 (1988). Three reprints submitted September 22, 1988.

3. (DOE/ER/04447-233) "Spectrophotometric Studies of Californium(III) Ions in Selected Lanthanide Trihalide Hosts" by W. R. Wilmarth, J. P. Young, R. G. Haire, and J. R. Peterson. Journal of the Less-Common Metals 143, 183-193 (1988). Three reprints submitted November 17, 1988.

4. (DOE/ER/04447-234) "The Raman Spectra of Polycrystalline Orthorhombic YF_3, SmF_3, HoF_3, YbF_3, and Single Crystal TbF_3" by W. R. Wilmarth, G. M. Begun, S. E. Nave, and J. R. Peterson. Journal of Chemical Physics 89, 711-715 (1988). Three reprints submitted August 11, 1988.

5. (DOE/ER/04447-235) "Raman and Absorption Spectrophotometric Studies of Selected Lanthanide, Californium-Doped Lanthanide, and Actinide Trihalides in the Solid State" by W. R. Wilmarth. Ph.D. Dissertation, University of Tennessee, Knoxville, March 1988. Three copies submitted April 4, 1988.

6. (DOE/ER/04447-236) "New Ternary Transuranium Compounds: Chalcogenide Halides" by T. L. Thevenin, W. R. Wilmarth, J. R. Peterson, and R. G. Haire. Materials Research Bulletin 23, 851-855 (1988). Three reprints submitted September 8, 1988.

7. (DOE/ER/04447-237) "Raman Spectrometric Studies of Selected Lanthanide Tribromides and Trichlorides" by J. F. Daniel. M.S. Thesis, University of Tennessee, Knoxville, March 1988. Three copies submitted April 5, 1988.

8. (DOE/ER/13865-001) "Absorption and Raman Spectrophotometric Studies of Actinide Compounds" by W. R. Wilmarth, J. P. Young, R. G. Haire, G. M. Begun, and J. R. Peterson. Abstract of paper for oral presentation at the 18th Journees des Actinides, Paris, France, April 20-22, 1988. Three copies submitted April 4, 1988.

9. (DOE/ER/13865-002) "Raman Spectroscopic Studies of Gadolinium Trichloride as a Function of Temperature" by J. F. Daniel, W. R. Wilmarth, G. M. Begun, and J. R. Peterson. Journal of Crystallographic and Spectroscopic Research 19, 39-49 (1989). Three reprints submitted March 15, 1989.

10. (DOE/ER/13865-003) "Spectroscopic Studies of $PrCl_3$ and $PrBr_3$ in the Solid State" by W. R. Wilmarth, G. M. Begun, and J. R. Peterson. Abstract of paper for poster presentation at the 18th Rare Earth Research Conference, Lake Geneva, Wisconsin, September 12-16, 1988. Three copies submitted May 31, 1988.

11. (DOE/ER/13865-004) "On the Solid State Absorption Spectra of CfF_3 and CfF_4, and the Stability of CfF_4" by R. G. Haire, J. P. Young, J. R. Peterson, and D. D. Ensor. Abstract of paper for poster presentation at the 18th Rare Earth Research Conference, Lake Geneva, Wisconsin, September 12-16, 1988. Three copies submitted May 31, 1988.

12. (DOE/ER/13865-005) "Raman Spectra of Selected Transuranium Trihalides in the Solid State" by W. R. Wilmarth, G. M. Begun, R. G. Haire, and J. R. Peterson. Journal of Chemical Physics 89, 4666-4670 (1988). Three reprints submitted November 28, 1988.

13. (DOE/ER/13865-006) "Spectroscopic Studies of $PrCl_3$ and $PrBr_3$ in the Solid State" by W. R. Wilmarth, G. M. Begun, and J. R. Peterson. Journal of the Less-Common Metals 148, 193-200 (1989). Three reprints submitted June 20, 1989.

14. (DOE/ER/13865-007) "The Effect of Pressure on the Raman and Absorption Spectra of $PrCl_3$, $PrBr_3$, and $NdBr_3$" by W. R. Wilmarth, G. M. Begun, R. G. Haire, J. P. Young, and J. R.

Peterson. Applied Spectroscopy 43, 1038-1045 (1989). Three reprints submitted October 5, 1989.

15. (DOE/ER/13865-008) "Physical-Chemical Studies of Transuranium Elements" by J. R. Peterson. Progress report for the period April 1, 1988 - March 31, 1989. Copies submitted November 29, 1988.

16. (DOE/ER/13865-009) "Characterization of Selected Solid-State Actinide Compounds via Raman Phonon Spectroscopy: Another Spectral Probe of Crystal Structure" by W. R. Wilmarth, G. M. Begun, G. D. Del Cul, R. G. Haire, and J. R. Peterson. Extended abstract of paper for poster presentation at the international conference ACTINIDES-89, Tashkent, USSR, September 24-29, 1989. Three copies submitted April 19, 1989.

17. (DOE/ER/13865-010) "Laser Excited Fluorescence Spectroscopy of Probe Ions for the Characterization of Crystal Site Symmetries in Lanthanide and Actinide Compounds" by G. M. Murray, R. V. Sarrio, O. L. Keller, and J. R. Peterson. Extended abstract of paper for oral presentation at the international conference ACTINIDES-89, Tashkent, USSR, September 24-29, 1989. Three copies submitted April 19, 1989.

18. (DOE/ER/13865-011) "On the Use of Spectroscopic Techniques to Determine the Crystal Structure of the Artificial f Elements" by J. R. Peterson. Abstract of paper for poster presentation at the 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 17-22, 1989. Three copies submitted August 11, 1989.

19. (DOE/ER/13865-012) "Molar Enthalpy of Formation of Californium Tribromide" by J. Fuger, R. G. Haire, W. R. Wilmarth, and J. R. Peterson. Journal of the Less-Common Metals 158, 99-104 (1990). Three reprints submitted April 20, 1990.

20. (DOE/ER/13865-013) "Absorption and Raman Spectrophotometric Studies of Lanthanide and Actinide Trihalides Under Pressure" by J. R. Peterson. Extended abstract of paper for oral presentation at the 3rd Workshop on Actinides Under Pressure, Karlsruhe, Federal Republic of Germany, July 24-25, 1989. Three copies submitted June 20, 1989.

21. (DOE/ER/13865-014) "The Effects of Hydration on the Luminescence Spectra of Trisodium Tris(2,6-pyridinedicarboxylato) europium(III) Compounds" by G. M. Murray, R. V. Sarrio, and J. R. Peterson. Inorganica Chimica Acta (in press). A preprint copy submitted July 6, 1990.

22. DOE/ER/13865-015) "Raman, Fluorescence and Absorption Spectroscopic Studies of Selected Lanthanide Oxychlorides (LnOCl)" by G. D. Del Cul, G. M. Murray, G. M. Begun, and J. R. Peterson. Abstract of paper for oral presentation at the 41st Southeast Regional American Chemical Society meeting, Winston-Salem, North Carolina, October 9-11, 1989. Three copies submitted August 10, 1989.

23. (DOE/ER/13865-016) "Absorption Spectrophotometric Study of $CfCl_3$ at Pressures up to 35 GPa" by J. P. Young, J. R. Peterson, R. G. Haire, W. R. Wilmarth, and G. M. Begun. High Pressure Research (in press). A preprint copy submitted February 7, 1990.

24. (DOE/ER/13865-017) "Raman Spectra of Some Actinide Dioxides and of EuF_2" by G. M. Begun, R. G. Haire, W. R. Wilmarth, and J. R. Peterson. Journal of the Less-Common Metals 162, 129-133 (1990). Three reprints submitted November 9, 1990.

25. (DOE/ER/13865-018) "Characterization of Selected Solid-State Actinide (and Related) Compounds via Raman and Absorption Spectrophotometry" by W. R. Wilmarth and J. R. Peterson. Handbook on the Physics and Chemistry of the Actinides, Volume 6 (in press). A preprint copy submitted September 29, 1989.

26. (DOE/ER/13865-019) "Use of Absorption Spectra to Determine Crystal Structure in f-Transition Element Compounds" by J. R. Peterson, J. P. Young, W. R. Wilmarth, and R. G. Haire. Applied Spectroscopy 44, 461-465 (1990). Three reprints submitted April 19, 1990.

27. (DOE/ER/13865-020) "Physical-Chemical Studies of Transuranium Elements" by J. R. Peterson. Progress report for the period April 1, 1989 - March 31, 1990. Copies submitted November 27, 1989.

28. (DOE/ER/13865-021) "Anti-Stokes Luminescence of ^{248}Curium(III) Bromide" by G. M. Murray, G. D. Del Cul, G. M. Begun, R. G. Haire, J. P. Young, and J. R. Peterson. Chemical Physics Letters 168, 473-476 (1990). Three reprints submitted July 31, 1990.

29. (DOE/ER/13865-022) "Correlation of Phonon Raman and Europium(III) Luminescence Spectra as a Probe of Structure in Trisodium Tris(2,6-pyridinedicarboxylato)lanthanide(III) Compounds" by G. M. Murray, R. V. Sarrio, and J. R. Peterson. Applied Spectroscopy (in press). A preprint copy submitted June 29, 1990.

30. (DOE/ER/13865-023) "Luminescence, Absorbance, and Raman Studies of EuOCl at Various Pressures" by G. D. Del Cul, G. M. Murray, S. E. Nave, C-T. P. Chang, G. M. Begun, and J. R. Peterson. Abstract of paper for poster presentation at the First International Conference on f Elements, Leuven, Belgium, September 4-7, 1990. Three copies submitted April 11, 1990.

31. (DOE/ER/13865-024) "Anti-Stokes Luminescence of Selected Actinide(III) Compounds" by G. D. Del Cul, G. M. Murray, S. E. Nave, C-T. P. Chang, R. G. Haire, and J. R. Peterson. Abstract of paper for poster presentation at the First International Conference on f Elements, Leuven, Belgium, September 4-7, 1990. Three copies submitted April 11, 1990.

32. (DOE/ER/13865-025) "The Transplutonium Elements: Research Opportunities and Challenges on the Edge of Matter" by J. R. Peterson. Abstract of paper for oral presentation at the 14th Annual Actinide Separations Conference, Gatlinburg, Tennessee, May 14-17, 1990. Three copies submitted April 20, 1990.

33. (DOE/ER/13865-026) "Luminescence, Absorbance and Raman Studies of EuOCl at Various Pressures" by G. D. Del Cul, G. M. Murray, S. E. Nave, C-T. P. Chang, G. M. Begun, and J. R. Peterson. European Journal of Solid State and Inorganic Chemistry (in press). A preprint copy submitted August 31, 1990.

34. (DOE/ER/13865-027) "Anti-Stokes Luminescence of Selected Actinide(III) Compounds" by G. M. Murray, G. D. Del Cul, S. E. Nave, C-T. P. Chang, R. G. Haire, and J. R. Peterson. European Journal of Solid State and Inorganic Chemistry (in press). A preprint copy submitted August 21, 1990.

35. (DOE/ER/13865-028) "Anti-Stokes Luminescence of Selected Curium Compounds" by G. M. Murray, G. D. Del Cul, G. M. Begun, J. P. Young, and J. R. Peterson. Abstract of paper for oral presentation at the 199th American Chemical Society meeting, Boston, Massachusetts, April 22-27, 1990. Three copies submitted June 22, 1990.

36. (DOE/ER/13865-029) "Luminescence, Raman and Absorption Spectrophotometric Studies of Selected Lanthanide and Actinide Compounds in the Solid State" by G. D. Del Cul. Ph.D. Dissertation, University of Tennessee, Knoxville, December 1990. Three copies submitted September 10, 1990.

In addition the principal investigator has co-authored the following documents which have been asssigned DOE document numbers based on other DOE contracts/grants:

1. (DOE/ER/13834-2) "Crystal-Field Anisotropy in the Magnetic Susceptibility of Single-Crystal $CfCl_3$" by J. R. Moore, S. E. Nave, R. C. Hart, W. R. Wilmarth, R. G. Haire, and J. R. Peterson. Physical Review B 38, 2695-2702 (1988).

2. (LA-UR-88-2759) "Spectroscopic and Redox Properties of Berkelium in Complexing Aqueous Carbonate and Citrate Solutions" by D. E. Hobart, D. E. Morris, P. D. Palmer, R. G. Haire, and J. R. Peterson. Radiochimica Acta 49, 119-124 (1990). Three reprints submitted June 28, 1990.

3. (LA-UR-88-2760) "Voltammetric Investigation of the Berkelium(IV/III) Couple in Concentrated Aqueous Carbonate Solutions" by D. E. Morris, D. E. Hobart, P. D. Palmer, R. G. Haire, and J. R. Peterson. Radiochimica Acta 49, 125-134 (1990). Three reprints submitted June 28, 1990.

During the current report period, research sponsored by this contract/grant was presented in oral or poster format at the following gatherings:

1. 18th Journees des Actinides, Paris, France, April 20-22, 1988. One oral, one poster; both contributed.

2. The University of Tennessee, Knoxville, Tennessee, June 23 and 24, 1988. Two oral; both invited.

3. Summer School for Nuclear and Radiochemistry, San Jose State University, San Jose, California, July 12, 1988. One oral; invited.

4. Lawrence Berkeley Laboratory, Berkeley, California, July 13, 1988. One oral; invited.

5. 18th Rare Earth Research Conference, Lake Geneva, Wisconsin, September 12-16, 1988. Three posters; all contributed.

6. Mercer University, Macon, Georgia, October 4, 1988. One oral; invited.

7. University of South Alabama, Mobile, Alabama, November 11, 1988. One oral; invited.

8. Spring Hill College, Mobile, Alabama, November 11, 1988. One oral; invited.

9. San Jose State University, San Jose, California, December 8, 1988. One oral; invited.

10. The University of Tennessee, Knoxville, Tennessee, June 15, 1989. One oral; invited.

11. 3rd Workshop on Actinides Under Pressure, Karlsruhe, Federal Republic of Germany, July 24-25, 1989. Two oral; both invited.

12. ACTINIDES-89, Tashkent, USSR, September 24-29, 1989. Two extended abstracts only; both contributed.

13. Middle Tennessee State University, Murfreesboro, Tennessee, October 5, 1989. One oral; invited.

14. 41st Southeast Regional American Chemical Society meeting, Winston-Salem, North Carolina, October 9-11, 1989. One oral; contributed.

15. Arkansas State University, Jonesboro, Arkansas, October 20, 1989. One oral; invited.

16. Rhodes College, Memphis, Tennessee, October 30, 1989. One oral; invited.

17. The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 17-22, 1989. One poster; contributed.

18. 199th American Chemical Society meeting, Boston, Massachusetts, April 22-27, 1990. One oral; invited.

19. 14th Annual Actinide Separations Conference, Gatlinburg, Tennessee, May 14-17, 1990. One oral; invited.

20. The University of Tennessee, Knoxville, Tennessee, June 28, 1990. One oral; invited.

21. Summer School for Nuclear and Radiochemistry, Brookhaven National Laboratory, Upton, New York, July 25, 1990. One oral; invited.

22. First International Conference on the f Elements, Leuven, Belgium, September 4-7, 1990. Two posters; both contributed.

23. The Robert A. Welch Foundation Conference on Chemical Research XXXIV. Fifty Years with Transuranium Elements, Houston, Texas, October 22-23, 1990. One oral; invited. Participation of the principal investigator in this event had to be cancelled because of the ill health of his wife.

MOLAR ENTHALPIES OF FORMATION OF $BaCmO_3$ AND $BaCfO_3$

J. Fuger[a] and R.G. Haire[b]

Introduction

Thermodynamic studies on perovskite-related complex oxides of several tetravalent lanthanides and actinides with barium and strontium have been published in recent years. Quantitative data on the molar enthalpies of formation exist for $BaCeO_3$ [1,2], $BaPrO_3$ [1], $BaTbO_3$ [1,2], $BaUO_3$ [3], $BaPuO_3$ [4], $BaAmO_3$ [2], $SrCeO_3$ [2], $SrTbO_3$ [2], and $SrAmO_3$ [2]. Morss et al. [1,3,4] showed that, for a number of barium compounds with the general formula $BaM'O_3$ (M' = Ti, Mo, Hf, Zr, Tb, Pr, U, or Pu), the enthalpy change $\Delta_r H^\circ_m$(complex), corresponding to the formation of these compounds from the binary oxides according to reaction (1)

$$BaO(cr) + M'O_2(cr) = BaM'O_3(cr), \qquad (1)$$

becomes less favorable as the Goldschmidt tolerance factor t [5] decreases. In fact, it was shown very recently [2] that a linear relationship existed between $\Delta_f H^\circ_m$(complex) and t that could be extended to analogous strontium compounds, especially those with cerium, terbium, and americium, which display a very distorted perovskite structure.

The purpose of the present study is to extend the correlation to $BaCmO_3$, and $BaCfO_3$, i.e., for the heaviest actinides for which such compounds can be prepared and to base on the best possible grounds estimation of the molar enthalpies of formation of other, some of them yet unprepared, homologous $MM'O_3$ compounds (M = Ba or Sr; M' = Th, Pa, Np, or Bk). Additionally, given adequate auxiliary data, the results on $BaCfO_3$ will provide information on the

molar enthalpy of formation of stoichiometric CfO_2 and on the Cf^{4+}/Cf^{3+} standard potential.

Experimental

The complex oxides were obtained by heating stoichiometric amounts of BaO and $^{248}CmO_2$ or $^{249}CfO_2$. Two preparations of $BaCmO_3$ (I and II) and one preparation of $BaCfO_3$ (I) were carried out. X-ray powder diffraction was used to characterize the samples.

All samples were handled in a gloved box whose helium atmosphere contained less than 1 ppm water and 10-100 ppm oxygen and nitrogen.

The techniques used for handling and weighing the samples for calorimetry have been recently described [7]. In each calorimetric run one to three pieces, detached from the bulk of the preparation, were used. The isoperibolic calorimeter, having a nominal capacity of 5 cm^3, has also been described [8], and the details of the verification of its performance have been published [8-10].

The selected dissolution medium was 1.000 ± 0.005 $mol \cdot dm^{-3}$ $HClO_4$ because, based on similar experiments [2] with $BaTbO_3$ and $SrTbO_3$, this medium is known to dissolve such compounds in a matter of a few minutes and because the non-complexing nature of the ClO_4^- ion simplifies the extrapolation of data to an infinitely dilute medium.

Uncertainty limits on the mean of several calorimetric measurements are based on the student t 95% confidence level. All measurements are reported for 298.15 ± 0.05 K and p° = 101.325 kPa. Unless otherwise specified, auxiliary data are those recommended by CODATA [11].

Results and Discussion

The X-ray powder patterns of both $BaCmO_3$ (2 preparations) and $BaCfO_3$ exhibited only lines which were indexed in the cubic (Fm3m) symmetry although it is well known from neutron powder diffraction and high resolution X-ray powder diffraction that these 4f and 5f barium perovskites are rhombohedrically or orthorhombically distorted [12-16].

The results of the dissolution of the two compounds, according to equation (2)

$$BaM'O_3(cr) + 5H^+(soln) =$$

$$[Ba^{2+} + M'^{3+} + 5/2\ H_2O](soln) + 1/4\ O_2(g) \quad \Delta H_2 = \Delta_{soln} H_m, \qquad (2)$$

where (soln) stands for 1.000 $mol \cdot dm^{-3}$ $HClO_4$ and M' = Cm or Cf are given in Table 1. As can be deduced from these data, the actinide concentration in the calorimetric solution was $\leq 10^{-3}$ $mol \cdot dm^{-3}$. Heat evolution upon dissolution was complete within 9-12 minutes in the case of the $BaCmO_3$ samples and within 5 minutes in the case of the $BaCfO_3$ samples. This difference in behavior, for which we have no explanation, leads to larger uncertainties in the calculation of the heat effect and is reflected in the larger uncertainty of the mean $BaCmO_3$ value as compared to that for $BaCfO_3$.

Although the evolution of gas (O_2) could be seen as expected from reaction (2), by observation under a microscope of the dissolution of a sample of $BaCmO_3$ in a small quantity of 1.000 $mol \cdot dm^{-3}$ $HClO_4$, we have no proof that this oxygen evolution was quantitative. Such a quantitative evolution of $O_2(g)$ would correspond to a small endothermic effect of 0.3 kJ per mole of dissolved oxide, due to the saturation of the gas by the water vapor at its equilibrium pressure [17] over 1.000 $mol \cdot dm^{-3}$ $HClO_4$. On the other hand, dissolution of 20% of the oxygen released in reaction (2) would correspond to

an exothermic effect of 0.55 kJ per mol of dissolved oxide [18, 19]. Under these circumstances no correction could be applied for these effects which, in any case, lead to an uncertainty which is much smaller than the uncertainty limits on the mean of the several identical experiments.

From the enthalpy of solution according to equation (2), the molar enthalpy of formation according to reaction (3)

$$Ba(cr) + M'(cr) + 3/2\ O_2(g) = BaM'O_3(cr) \qquad \Delta H_3 = \Delta_f H^\circ_m(BaM'O_3, cr) \qquad (3)$$

can be obtained through the use of the following reactions, all in 1.000 $mol \cdot dm^{-3}$ $HClO_4$, referred to as (soln),

$$M'(cr) + 3H^+(soln) = M'^{3+}(soln) + 3/2\ H_2(g) \qquad \Delta H_4 \qquad (4)$$

$$Ba(cr) + 2H^+(soln) = Ba^{2+}(soln) + H_2(g) \qquad \Delta H_5 \qquad (5)$$

$$5/2\ H_2(g) + 5/4\ O_2(g) + [Ba^{2+} + M'^{3+}](soln) = [Ba^{2+} + M'^{3+} + 5/2\ H_2O](soln) \qquad \Delta H_6 \qquad (6)$$

Thus, $\Delta H_3 = \Delta_f H^\circ_m(BaM'O_3,\ cr) = \Delta H_4 + \Delta H_5 + \Delta H_6 - \Delta H_2$ (7)

The standard molar enthalpies of formation of Cm^{3+} (aq) and Cf^{3+} (aq) have been reported as $-(615 \pm 5)$ $kJ \cdot mol^{-1}$ [20] and $-(577 \pm 5)$ $kJ \cdot mol^{-1}$ [10], respectively. Making the reasonable assumption that these enthalpies change negligibly between 1 $mol \cdot dm^{-3}$ $HClO_4$ and standard conditions, we have, for ΔH_4

$$\Delta_f H_m(Cm^{3+},\ soln) = -(615 \pm 5)\ kJ \cdot mol^{-1}$$

and

$$\Delta_f H_m(Cf^{3+},\ soln) = -(577 \pm 5)\ kJ \cdot mol^{-1}$$

Similarly, we will take $\Delta H_5 = \Delta_f H_m(Ba^{2+},\ soln) = -(533.5 \pm 1.7)$ $kJ \cdot mol^{-1}$, a value identical to that accepted for standard conditions [21]. Finally we take $\Delta H_6 = -5/2\ (285.84 \pm 0.04)$ $kJ \cdot mol^{-1}$ from the standard molar enthalpy of formation of water [11] and the relative partial molar enthalpy of water [22] in 1.000 $mol \cdot dm^{-3}$ $HClO_4$, assuming negligible the influence of small ($< 10^{-3}$

mol·dm^{-3}) concentrations of Ba^{2+} and M'^{3+}. Thus, we obtain $\Delta_f H°_m(BaCmO_3, cr)$ = -(1517.8 ± 7.1) kJ·mol^{-1} and $\Delta_f H°_m(BaCfO_3, cr)$ = -(1477.9 ± 5.6) kJ·mol^{-1}.

From the experimental values $\Delta_f H°_m(BaO, cr)$ = -(548.0 ± 2.0) kJ·mol^{-1} [23] and $\Delta_f H°_m(CmO_2, cr)$ = -(911 ± 6) kJ·mol^{-1}, we can calculate, as we have done [2] for analogous compounds, $\Delta_r H°_m$(complex) according to reaction (1). We obtain, for $BaCmO_3$, $\Delta_r H°_m$(complex) = -(588 ± 9.5) kJ·mol^{-1}. Use of this result together with the corresponding values published [2] for various $MM'O_3$ compounds (M = Ba, M' = Ti, Hf, Zr, Tb, Am, Pu, Ce, or U; M = Sr, M' = Ti, Mo, Zr, Tb, Am, or Ce) in conjunction with the Goldschmidt tolerance factor t, calculated from the ionic radii from Shannon [6], lead to relationship (8)

$$\Delta_r H°_m(\text{complex}) = 800.4 - 10005\ t\ (\text{kJ}\cdot\text{mol}^{-1}) \qquad (8)$$

which, over the range $0.8 < t < 1$, fits the experimental results for all the above-listed compounds with an average standard deviation of 8.5 kJ·mol^{-1}. This result is quite satisfactory given the uncertainties in the ionic radii, and the slight variations in the crystal structure of the compounds.

From relationship (8), the ionic radii [6], and the standard molar enthalpies of formation of the various actinide dioxides [24], of BaO, given above, and of SrO, as -(590.53 ± 1.00) kJ·mol^{-2} [25], we can estimate the molar enthalpies of formation of several complex oxides for which no thermochemical data exist; these values are given in Table 2. The data we obtain for the $\Delta_r H°_m$(complex) in the case of $BaThO_3$ is distinctly more negative than that, -20 kJ·mol^{-1}, estimated by Williams et al. [3]. On the other hand it appears there is little hope to obtain in pure form any $SrM'O_3$ compounds for actinides lighter than neptunium, although the existence of these compounds (Pa-Pu) has been claimed [26].

Equation (8) can be used to estimate $\Delta_f H°_m(CfO_2, cr)$ based on the above reported $\Delta_f H°_m(BaCfO_3, cr) = (-1477.9 \pm 5.6)$ kJ·mol^{-1}. With $r_{Cf^{4+}} = 0.821$ Å, t = 0.876 and $\Delta_r H°_m(complex) = -(80.0 \pm 8.5)$ kJ·mol^{-1}, we obtain $\Delta_f H°_m(CfO_2, cr) = -(850 \pm 10)$ kJ·mol^{-1}. This value is in very good agreement with that, -858 kJ·mol^{-1}, estimated by Morss [27] based on interrelationships between the molar volumes of the lanthanide and actinide dioxides and their standard molar enthalpies of solution.

An extrapolation to californium of the plot $(\Delta_f H°_m(M'O_2, cr) - \Delta_f H°_m(M'^{4+}, aq))$ as a function of the actinide and lanthanide tetravalent ionic radii [25] leads to $(\Delta_f H°_m(CfO_2, cr) - \Delta_f H°_m(Cf^{4+}, aq)) = -(549 \pm 5)$ kJ·mol^{-1} and yields $\Delta_f H°_m(M'^{4+}, aq) = -(301 \pm 11)$ kJ·mol^{-1}, compared to -313 estimated by Morss [27]. Finally, using the entropy values listed by this latter author, accepting an uncertainty of ± 20 J·K^{-1}·mol^{-1} for the difference $(S°(Cf^{4+}, aq) - S°(Cf^{3+}, aq))$, and $S°(H_2, g) = (130.571 \pm 0.005)$ J·K^{-1}·mol^{-1} [11], we obtain $E°(Cf^{4+}/Cf^{3+}) = (3.32 \pm 0.14)$ V for the standard potential of the Cf^{4+}/Cf^{3+} couple. This value is virtually identical to that, 3.2 V, listed by Morss [27], but is based on the first experimental thermochemical results on a solid tetravalent californium compound.

Summary

The enthalpies of solution in 1.00 mol·dm^{-3} $HClO_4$ of $BaCmO_3$ and $BaCfO_3$ were measured at 298.15 ±0.05 K and p° = 101.325 kPa as $-(345.3 \pm 4.7)$ and $-(347.2 \pm 1.9)$ kJ·mol^{-1}, respectively. The resulting standard molar enthalpies of formation, $\Delta_f H°_m(BaCmO_3, cr) = -(1517.8 \pm 7.1)$ kJ·mol^{-1} and $\Delta_f H°_m(BaCfO_3, cr) = -(1477.9 \pm 5.6)$ kJ·mol^{-1}, together with other corresponding experimental values for several lanthanide, actinide, and transition metal complex oxides with barium and strontium, are used to estimate the molar enthalpies of

formation of a number of actinide homologous compounds. The present results also provide additional information on the standard molar enthalpy of formation of CfO_2 and on the Cf^{4+}/Cf^{3+} standard potential.

References

[a] Visiting Professor of Chemistry. Permanent address: Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2340, D-7500, Karlsruhe, Germany.

[b] Chemistry Division, Oak Ridge National Laboratory.

1. L. R. Morss and N. Mensi, in G. J. McCarthy, H. B. Silber, and J. J. Rhyne (eds), The Rare Earths in Modern Science and Technology, Plenum: New York (1982) 297.

2. J. Goudiakas, R. G. Haire, and J. Fuger, *J. Chem. Thermodyn.*, *22* (1990) 577.

3. C. W. Williams, L. R. Morss, and I.-K. Choi, in G. S. Barney, J. D. Navratil, and W. W. Schulz (eds), Geochemical Behavior of Disposed Radioactive Waste, ACS Symposium Series No. 264: Washington, D.C. (1983) 323.

4. L. R. Morss and P. G. Eller, *Radiochim. Acta*, *47* (1989) 51.

5. J. B. Goodenough and J. M. Lango, Landolt-Bornstein Tables, Group III, Vol. 4a, Springer: Berlin (1970) 126.

6. R. D. Shannon, *Acta Cryst. A32* (1976) 751.

7. J. Fuger, R. G. Haire, W. R. Wilmarth, and J. R. Peterson, *J. Less-Common Metals*, *158* (1990) 99.

8. D. L. Raschella, Ph.D. Dissertation, University of Tennessee, Knoxville, TN (1978) (U.S. Department of Energy Document ORO-4447-081); D. L. Raschella, R. L. Fellows, and J. R. Peterson, *J. Chem. Thermodyn.*, *13* (1981) 303.

9. J. Fuger, R. G. Haire, and J. R. Peterson, *J. Inorg. Nucl. Chem.* *43* (1981) 3209.

10. J. Fuger, R. G. Haire, and J. R. Peterson, *J. Less-Common Metals*, *98* (1984) 315.

11. J. D. Cox, D. D. Wagman, and V. A. Medvedev (eds) CODATA Key Values for Thermodynamics, Hemisphere: New York (1988).

12. A. J. Jacobson, B. C. Tofield, and B. E. F. Fender, *Acta Cryst.*, *B28* (1972) 956.

13. M. Danelon Mastromonaco, I. Barbarrol, and A. Cocco, *Ann. Chim. Rome*, *59* (1959) 465.

14. T. Nakamura, *Chem. Lett.* (1974) 429.

15. J. A. Barret, A. J. Jacobson, B. C. Tofield, and B. E. F. Fender, *Acta Cryst.*, *B38* (1982) 2775.

16. G. G. Christoph, A. C. Larson, P. G. Eller, J. D. Purson, J. D. Zahrt, R. A. Penneman, and G. H. Rhinehart, *Acta Cryst.*, *B44* (1988) 575.

17. E. D. Washburn, C. J. West, N. E. Dorsey, F. R. Bischowsky, and A. D. Klemenc (eds), International Critical Tables, Vol. III, McGraw Hill: New York (1928).

18. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumnn, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data.*, *11* (1982) Supplements.

19. G. Geffcken, *Z. Phys. Chemie*, *49* (1904) 257.

20. J. Fuger, J. Reul, and W. Müller, *Inorg. Nucl. Chem. Lett.*, *11* (1975) 265.

21. L. R. Morss and C. W. Williams, *J. Chem. Thermodyn.*, *15* (1983) 279.

22. V. B. Parker, Natl. Bur. Stand. (U.S.) Report NSRDS-NBS-2 (1965).

23. G. C. Fitzgibbon, E. J. Huber, Jr., and C. E. Holley, Jr., *J. Chem. Thermodyn.*, *5* (1973) 577.

24. J. Fuger, in N. Edelstein (ed), Actinides in Perspective, Pergamon: Oxford (1982) 409.

25. I. J. Brink and C. E. Holley, Jr., *J. Chem. Thermodyn.*, *10* (1978) 259.

26. C. Keller, in MTP, Review of Science, Vol 7, *Lanthanides and Actinides*, K. W. Bagnall (ed), Butterworth: London (1972).

27. L. R. Morss, in J. J. Katz, G. T. Seaborg, and L. R. Morss (eds), The Chemistry of the Actinide Elements, 2nd Ed., Chapman and Hall: London (1986) Chapter XVII, p. 1278.

Table 1.

Molar enthalpy of solution of $BaCmO_3$ and $BaCfO_3$ in 5.00 cm^3 of 1.000 $mol \bullet dm^{-3}$ $HClO_4$ at 298.15 ± 0.05 K and p° = 101.325 kPa.

Sample and Preparation Number	Sample Mass (μg)	ΔH^a (J)	$\Delta_{soln} H_m$ ($kJ \bullet mol^{-1}$)
$BaCmO_3$			
I	568.0	0.4563	-348.2
I	532.0	0.4184	-340.9
II	1144	0.9312	-352.8
II	1463	1.1539	-342.1
II	2112	1.6734	-343.3
II	1402	1.1148	-344.6
		Mean	-(345.3 ± 4.7)[b]
$BaCfO_3$			
I	869.7	0.6934	-346.3
I	566.7	0.4539	-347.9
I	908.3	0.7249	-346.7
I	622.0	0.5020	-350.6
I	753.0	0.6005	-346.4
I	1001.9	0.7969	-345.5
		Mean	-(347.2 ± 1.9)[b]

[a] Corrected for ampoule breaking and evaporation of solvent into the helium gas in the ampoule.

[b] 95% confidence level.

Table 2.

Estimated molar enthalpies of formation for a number of barium and strontium complex oxides with actinides.

$BaM'O_3$ (cr)				
M'	$\Delta_f H^\circ_m$ ($M'O_2$, cr) ($kJ \cdot mol^{-1}$) [from ref. 24]	t	$\Delta_r H^\circ_m$(complex) ($kJ \cdot mol^{-1}$) [from equation (8)]	$\Delta_f H^\circ_m$($BaM'O_3$, cr) ($kJ \cdot mol^{-1}$)
Th	-(1226.7 ± 1.7)	0.831	-34.8	-(17399 ± 8.9)
Pa	-(1109 ± 15)	0.845	-48.8	-(1608 ± 17)
U	-(1084.9 ± 0.8)			
Np	-(1074.0 ± 2.5)	0.857	-60.9	-(1561.1 ± 9.1)
Pu	-(1056.2 ± 2.7)			
Cm	-(911 ± 6)			
Bk	-(1026 ± 9)	0.872	-76.0	-(1498 ± 13)

$SrM'O_3$ (cr)			
	t	$\Delta_r H^\circ_m$(complex) ($kJ \cdot mol^{-1}$) [from equation (8)]	$\Delta_f H^\circ_m$($SrMo_3$, cr) ($kJ \cdot mol^{-1}$)
Th	0.780	+16.5	-
Pa	0.793	+3.4	-
U	0.797	-0.6	-
Np	0.804	-7.6	-(1656.9 ± 8.9)
Pu	0.807	-10.6	-(1636.1 ± 9.0)
Cm	0.811	-14.7	-(1487 ± 10)
Bk	0.818	-21.8	-(1595 ± 12)

LUMINESCENCE, ABSORBANCE AND RAMAN STUDIES OF EUROPIUM OXYCHLORIDE AT VARIOUS PRESSURES

G. D. Del Cul, G. M. Murray, S. E. Nave,[a]
C-T. P. Chang,[a] and G. M. Begun[b]

Introduction

The use of lanthanide compounds as phosphors has produced a considerable literature concerning their optical properties. These properties are strongly influenced by the crystal structures of the respective compounds which normally change across a series of homologous lanthanide compounds, owing to the change in the lanthanide ion's size. The nature of the changes in the coordination polyhedron and crystal field parameters is normally obtained by observing a spectroscopic probe ion dispersed in spectroscopically inactive compounds. An alternative way of observing and examining structural changes is by the application of pressure. The application of pressure causes structural changes analogous to those produced by the substitution of differing lanthanide ions without the ambiguity of probe ion assimilation. Pressure studies can also be used to investigate new synthesis methods and the delocalization of f electrons.

Experimental

The single crystals of EuOCl were prepared by flux growth from a melt of anhydrous $EuCl_3$ [1]. The crystal structure of each sample examined in this work was verified by X-ray diffraction and by a Raman crystal phonon technique [2]. The instruments used for the luminescence, absorbance and Raman spectroscopic studies have been described previously [3,4]. Luminescence from the $^5D_{2,3}$ levels in Eu^{3+} was obtained by resonance enhanced two-photon

excitation in the same manner as Hölsä [5]. The equipment and methodology for the pressure studies have been described previously [4].

Results and Discussion

The UV-VIS spectra of lanthanide ions in solid compounds consist of weak, narrow, intra-4f level transitions at low energies and strong, broad, inter-level or charge transfer transitions at higher energies. The positions of these two spectral forms, relative to visible light, are dependent on the oxidation state of the lanthanide ion. Normally Ln^{3+} ions exhibit narrow lines in the entire visible wavelength region, while Ln^{2+} ions have broad features in the blue to green and perhaps some narrow features in the far red. When a lanthanide ion is placed in a crystal field, the atomic free ion levels will split into a number of sublevels that can be characterized by the irreducible representation of the appropriate point group describing the crystal field symmetry about that ion. In this manner the narrow, intra-4f transitions are split into groups, or manifolds, whose pattern reflects the coordination polyhedron about the lanthanide ion.

The crystal structure of EuOCl is the PbFCl type ($P_{4/nmm}$; D^7_{4h}) with the Eu^{3+} ions residing in sites with C_{4v} point symmetry [6]. The relative intensities of the lines in a given manifold will be roughly equal to the degeneracy of the irreducible representation characteristic of the respective transition. For C_{4v} site symmetry the transitions of the Eu^{3+} ion are either singly or doubly degenerate. The luminescence spectrum exhibited by the Eu^{3+} ion in EuOCl, under ambient to low applied pressure, corresponds very well to the spectrum expected from an Eu^{3+} ion in a crystal field of C_{4v} symmetry. The predominant luminescence produced by the Eu^{3+} ion results from transitions originating in the $^5D_0$ excited electronic state relaxing to the lower $^7F_{0-6}$

levels. The luminescence spectrum exhibited by Eu^{3+} in EuOCl at ambient or low applied pressure is illustrated in Figure 1.

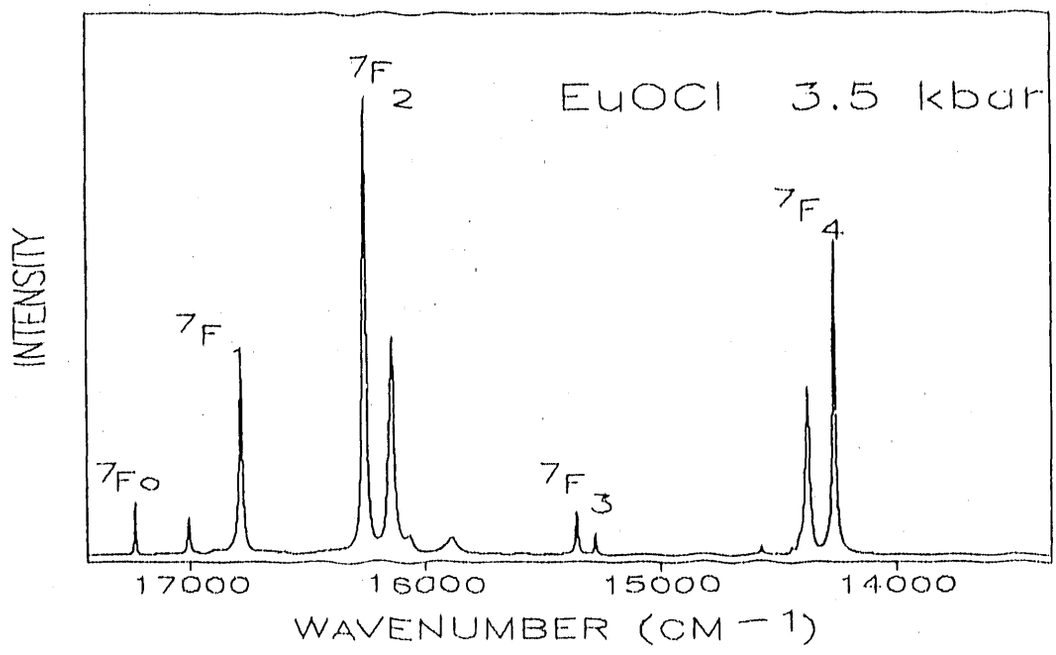

Fig. 1. Luminescence spectrum of EuOCL showing emission from the $^5D_0$ level to the $^7F_{0-4}$ levels.

As stated above, Ln^{2+} ions can be expected to exhibit strong, broad transitions in the visible wavelength region. In the case of Eu^{2+} ion, the peak of the band in the visible region occurs at about 18000 cm^{-1}. The luminescence spectrum of a representative Eu^{2+} compound, $EuCl_2$, is shown in Figure 2. Also seen in Figure 2 are luminescence spectra of EuOCl at moderate pressures, 48 and 112 kbar. The f→f transitions are red-shifted with increased pressure due to compression of the electronic cloud and, conceivably, increased covalency. It is apparent in Figure 2 that the narrow, intra-4f transitions are becoming obscured by a broad, strong, emission band in the energy region for Eu^{2+} ion emission. Examination of the sample at elevated pressure, by light microscopy, showed the crystals becoming brown and

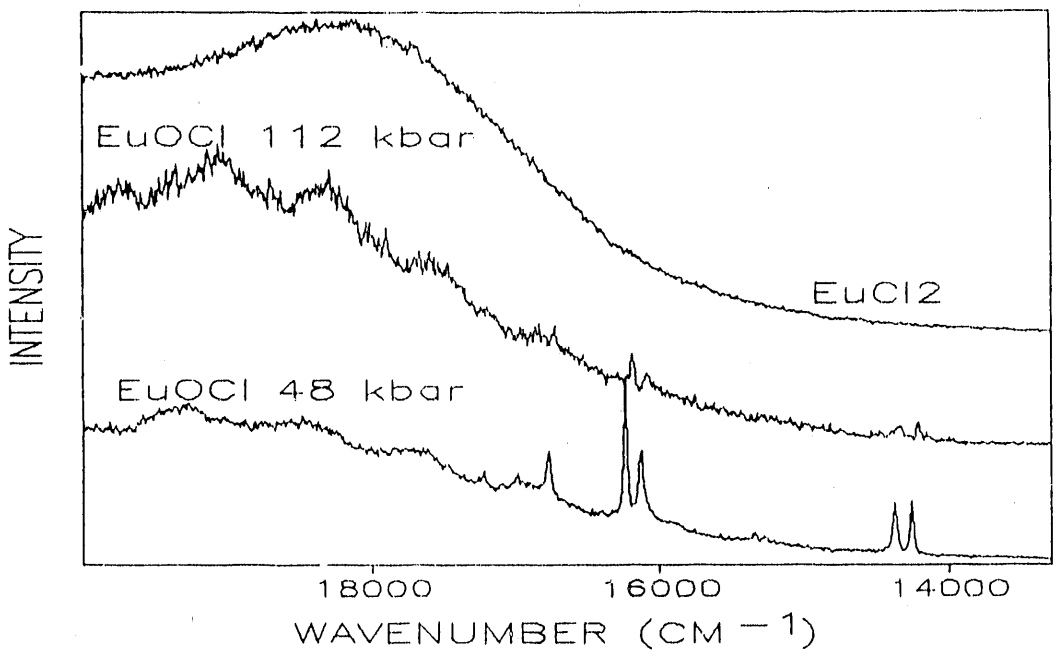

Fig. 2. Luminescence spectra of EuOCl at elevated pressure and of $EuCl_2$ at ambient pressure.

slightly opaque. The incremental application of pressure was repeated with simultaneous measurement of luminescence lifetimes. The results of these measurements are given in Table I. Concurrent with the rise in broadband emission there is a decrease in the radiative lifetime. All these observations are reversible with pressure.

Table I
Radiative Lifetime Versus Pressure for EuOCl

Pressure (kbar)	Lifetime $t_{1/2}$ (μs)
0.0	15.5
3.2	12.6
6.6	7.8
12.6	7.2
53.6	5.6

The absorption spectra obtained from EuOCl at elevated pressures still showed the characteristic Eu^{3+} peaks, although they were weakened because of the shorter light path due to gradual thinning and diminishing transparency of

the sample with increased pressure. The absorption peaks are also broadened by the application of pressure. Thus, the presence of Eu^{2+} ions in an EuOCl sample under pressure cannot be determined precisely from the absorption spectra obtained using our single-beam microscope spectrophotometer.

In addition to the luminescence and absorbance studies, an attempt was made to acquire further information from analysis of the Raman phonon spectra of EuOCl under pressure, but these spectra were too weak and broad to be useful. Because a measurement of the magnetic moment or the Mössbauer spectrum at elevated pressure remains as yet unfeasible, it is uncertain whether the apparent reduction of Eu^{3+} to Eu^{2+} is a bulk process or a surface phenomenon. This apparent reduction, reversible with pressure, is probably the result of shifting electron density from the anionic environment toward the Eu^{3+} ions with increased pressure.

References

[a] Physics Department, University of Tennessee.

[b] Chemistry Division, Oak Ridge National Laboratory.

1. J. Aride, J-P. Chaminade, and M. Pouchard, *J. Crystal Growth*, 1982, **57**, p. 194.

2. W. Wilmarth, G. Begun, R. Haire, and J. Peterson, *J. Chem. Phys.*, 1988, **89**, p. 4666.

3. G. Murray, G. Del Cul, G. Begun, R. Haire, J. Young, and J. Peterson, *Chem. Phys. Letters*, 1990, **168**, p. 473.

4. W. Wilmarth, G. Begun, R. Haire, J. Young, and J. Peterson, *Appl. Spectrosc.*, 1989, **43**, p. 1038.

5. J. Hölsä, *Chem. Phys. Letters*, 1984, **121**, p. 246.

6. P. Caro, *J. Less-Common Metals*, 1968, **16**, p. 367.

ANTI-STOKES LUMINESCENCE OF SELECTED ACTINIDE(III) COMPOUNDS

G. M. Murray, G. D. Del Cul, S. E. Nave,[a]
C-T. P. Chang,[a] and R. G. Haire[b]

Introduction

Anti-Stokes luminescence from lanthanide and lanthanide-doped compounds has been studied extensively [1]. The mechanisms described for these processes involve simultaneous, two photon absorption [2], ion-ion interactions [2], and sequential or resonance-assisted two photon absorption [3]. The sequential or resonance-assisted route may employ one or more colors for excitation.

The present work is the result of a search for a technique to observe weak luminescence from a large number of different lanthanide and actinide excited states. Such luminescence is often weak due to efficient, non-radiative decay from closely spaced excited levels. However, because of the low background produced by sequential two photon excitation, the energies (and polarizations) of many more levels can be obtained. These energy values are useful in calculating crystal field parameters and in determining lanthanide and actinide ion site symmetries.

Experimental

The actinide isotopes used in this work were produced in the High Flux Isotope Reactor and were processed and purified using standard solvent extraction and/or ion exchange techniques [4]. The anhydrous compounds were prepared by microchemical techniques that have been described elsewhere [5]. The crystal structure of each sample examined in this work was verified by a Raman crystal phonon technique [6]. The instrumentation used to acquire the Raman and luminescence spectra has been described previously [7].

Results and Discussion

A group theoretical analysis predicts that the various free ion electronic levels will be split into (J + 1/2) Stark components for all Kramers ions in non-cubic symmetry [8]. Since the ground state of the Cm^{3+} ion is, in Russell-Saunders notation, an S state, it is not expected to exhibit a significant crystal field splitting (values obtained for $LaCl_3:Cm^{3+}$ show components split by less than 1 cm^{-1}) [9]. Therefore the Cm(III) ion spectra will normally consist of groups of two or more lines, the intragroup lines separated about 100 cm^{-1} and the groups of lines separated about 1000 cm^{-1}, beginning at about 16500 cm^{-1} and extending to higher energy. An example of anti-Stokes luminescence from a curium compound ($^{248}CmI_3$) is shown in Figure 1. In the case of Cf(III) ion, the ground state is $^6H_{15/2}$ and the ground state splitting is about 300 cm^{-1}. The Cf(III) ion luminescence spectra are composed of complex groups of lines, with band spreads at least 300 cm^{-1} and the bands themselves separated by about 1000 cm^{-1}. An example of anti-Stokes luminescence from Cf(III) ion (≈5% Cf^{3+} in $LuCl_3$) is given in Figure 2.

The mechanism for the two photon, sequentially excited, Cm(III) ion luminescence is as follows. A large energy gap between the ground state and the first excited Stark manifold results in the excited state possessing a relatively long lifetime (≈10.0 μsec). This long lifetime facilitates the absorption of a second photon, further exciting the Cm^{3+} ion to a high lying, intra-5f level. The absorption of the second photon is followed by rapid multiphonon de-excitation to lower lying excited states which luminesce. Since excitation by two photons is very specific to the Cm^{3+} ion, background from scattered radiation and matrix luminescence are virtually eliminated. Therefore, the two photon absorption process allows observation of Cm^{3+} ion luminescence from excited states which previously were seen only by absorbance

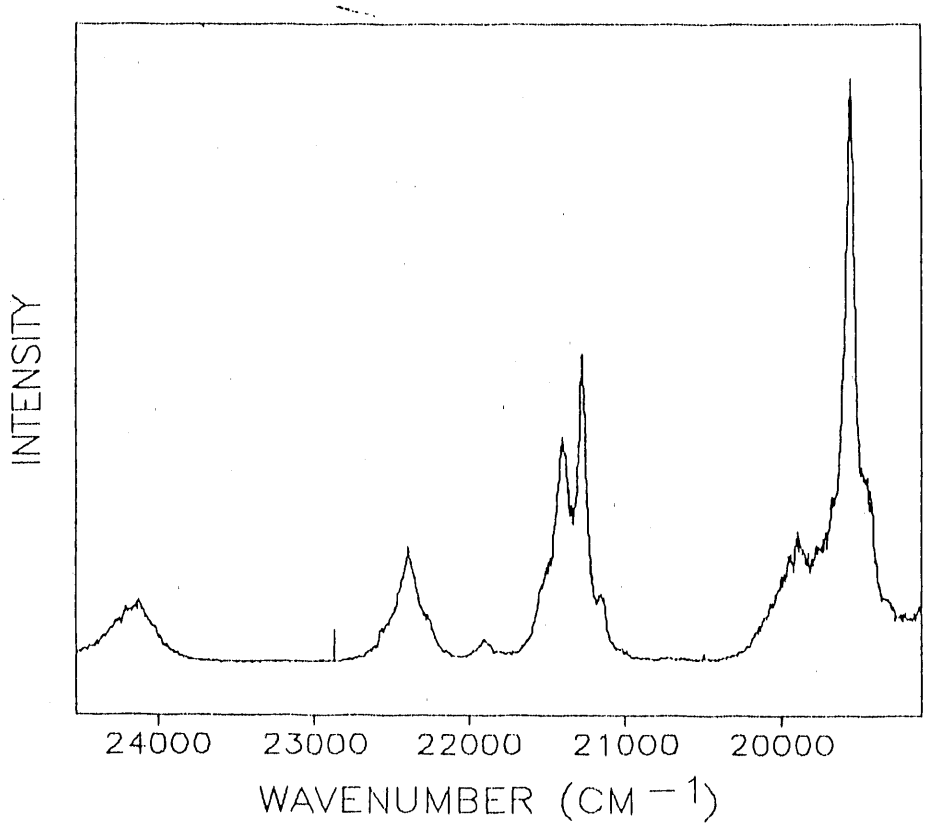

Fig. 1. Anti-Stokes luminescence spectrum of $^{248}CmI_3$ excited at 16345 cm^{-1}.

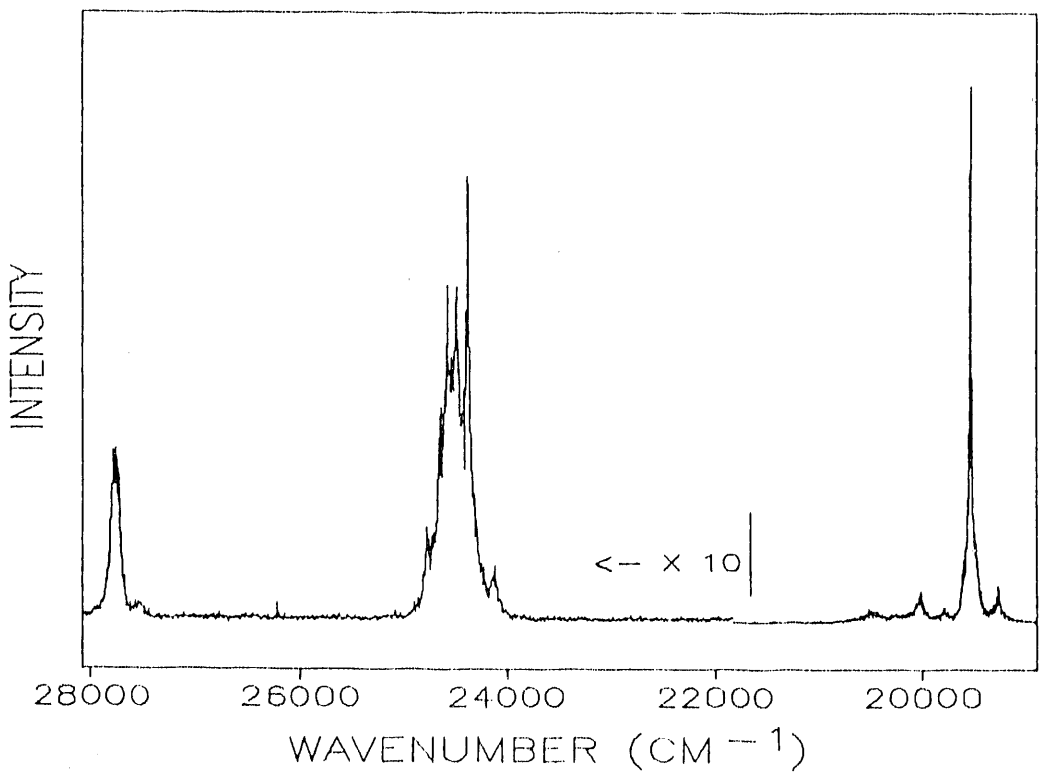

Fig. 2. Anti-Stokes luminescence spectrum of $LuCl_3:Cf^{3+}$ excited at 15850 cm^{-1}.

measurements. In Cf(III) ion there exist many more low lying levels than there are in Cm(III). Therefore, exciting Cf(III) ion as a dopant to reduce Cf(III) ion-ion interactions facilitates the observation of anti-Stokes luminescence in the visible wavelength range. The demonstration of anti-Stokes luminescence from Cf(III) ion and Cm(III) ion suggests that anti-Stokes luminescence should occur from other An(III) ions as well.

References

[a] Physics Department, University of Tennessee.

[b] Chemistry Division, Oak Ridge National Laboratory.

1. F. Auzel, *Compt. Acad. Sci.*, 1966, **B262**, p. 1016.

2. M. Downer, in W. Yen (ed.), "Laser Spectroscopy of Solids II", Springer-Verlag, Berlin, 1989, p. 29.

3. J. Hölsä, *Chem. Phys. Letters*, 1984, **112**, p. 246.

4. L. King, J. Bigelow, and E. Collins, in J. Navratil and W. Schulz (eds.), "Transplutonium Elements - Production and Recovery", ACS Symposium Series 161, American Chemical Society, Washington, 1981, p. 133.

5. J. Young, R. Haire, R. Fellows, and J. Peterson, *J. Radioanal. Chem.*, 1978, **43**, p. 479.

6. W. Wilmarth, G. Begun, R. Haire, and J. Peterson, *J. Chem. Phys.*, 1988, **89**, p. 4666.

7. G. Murray, G. Del Cul, G. Begun, R. Haire, J. Young, and J. Peterson, *Chem. Phys. Letters*, 1990, **168**, p. 473.

8. G. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals", Interscience Publishers, New York, 1968; S. Hufner, "Optical Spectra of Transparent Rare Earth Compounds", Academic Press, New York, 1978.

9. J. Gruger, W. Cochran, J. Conway, and A. Nichol, *J. Chem. Phys.*, 1966, **45**, p. 1423.

END

DATE FILMED

02 / 05 / 91