

**NOTICE**

**PORTIONS OF THIS REPORT ARE ILLEGIBLE. IT**

has been reproduced from the best available copy to permit the broadest possible availability.

UCRL--90026

DE84 016174

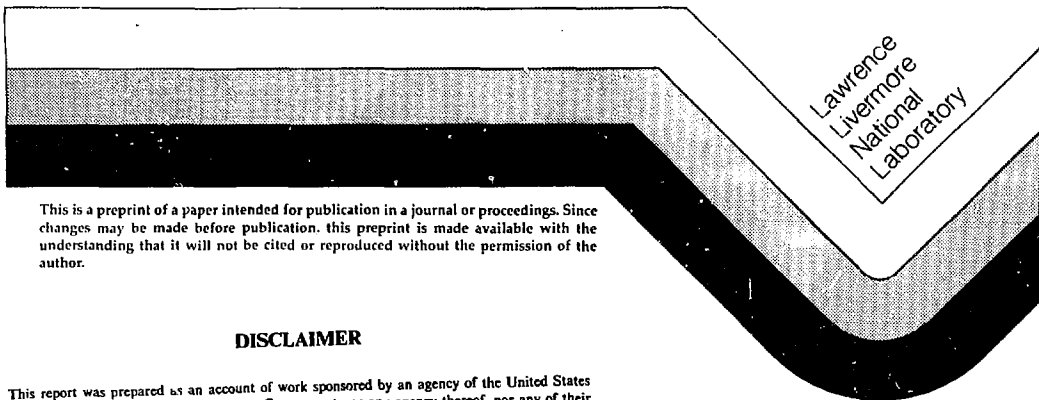
**CATHODOLUMINESCENCE OF URANIUM OXIDES**

K. Winer  
C. Colmenares  
F. Wooten

This paper was prepared for submittal to  
International Conference on Luminescence  
Madison, Wisconsin  
Aug. 13-17, 1984

**MASTER**

August 9, 1984



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

**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.

DISSEMINATION OF THIS DOCUMENT IS UNLIMITED

*John*

## CATHODOLUMINESCENCE OF URANIUM OXIDES\*

K. WINER

Lawrence Livermore National Laboratory and Department of Applied Science,  
University of California, P.O. Box 808, L-311, Livermore, CA 94550

C. COLMENARES

Lawrence Livermore National Laboratory, Livermore, CA 94550

F. WOOTEN

Department of Applied Science, University of California, Davis/Livermore,  
CA 94550

The cathodoluminescence of uranium oxide surfaces prepared *in-situ* from clean uranium exposed to dry oxygen was studied. The broad asymmetric peak observed at 470 nm is attributed to F-center excitation.

### 1. INTRODUCTION

The characterization of the defect structure of uranium oxides is essential to the understanding of the oxidation mechanisms of uranium. Uranium oxides have been studied for more than fifty years,<sup>1,2</sup> yet the understanding of their defect structure is incomplete. The oxidation of stoichiometric  $UO_2$  is thought to involve the incorporation of excess oxygen into the host fluorite lattice through the formation of defect clusters.<sup>3,4</sup> These clusters are randomly distributed throughout the oxide for low values of  $x$  in hyperstoichiometric  $UO_{2+x}$ . As  $x$  approaches 0.25, these clusters form chains which eventually become ordered to produce  $U_4O_9$ .<sup>5</sup>

Although uranium oxides have been studied with a variety of techniques,<sup>2,6,7</sup> the luminescence of these materials has not been systematically investigated. Therefore we have undertaken a detailed study of the luminescence properties of uranium oxide surfaces to understand their defect structure. Preliminary results for cathodoluminescence are described here.

### 2. EXPERIMENTAL METHODS

Samples were prepared in a standard ultrahigh vacuum system with a base pressure of less than  $2 \times 10^{-8}$  Pa. High purity (< 100 ppm metallic impurities) polycrystalline uranium samples were cleaned by argon ion bombardment at 1073K to remove surface impurities. The clean uranium was then exposed to increasing amounts of high purity dry oxygen. Exposure times and

\*Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

pressures were chosen to produce distinct stoichiometries and are listed in Table 1.

Table 1: Dry Oxygen Exposures

Exposure	Stoichiometry	Reference
a) 2 min. @ $1.3 \times 10^{-4}$ Pa	$UO_{2-x}$	9
b) 30 min. @ $1.3 \times 10^{-4}$ Pa	$UO_2$	7
c) 20 hrs. @ 0.7 Pa	$UO_{2+x}$	7

Cathodoluminescence spectra were taken after each exposure. The cathodoluminescence was excited with 5 KeV electrons from a grazing incidence gun with beam currents of  $\sim 125 \mu A$ . The luminescence was collected by a quartz lens optical telescope and passed through a grating spectrograph to a fast scan diode array backed by a channel plate. Spectra were stored in a minicomputer for subsequent analysis. Both the oxygen exposures and the luminescence measurements were performed at room temperature.

### 3. RESULTS

The luminescence spectra for the three exposures are shown in figure 1. The peak position remained at 470 nm for each spectrum although the intensity decreased with increasing exposure.

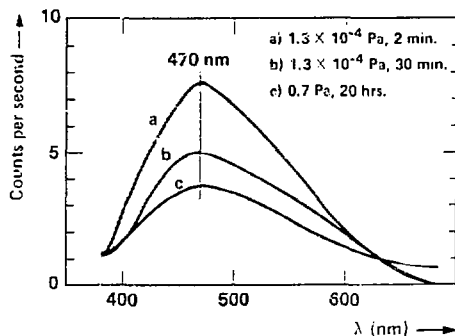


Fig 1. Cathodoluminescence spectra for dry oxygen exposures of a) 120 L (3 monolayers), b) 1800 L (45 monolayers) and c)  $3 \times 10^8$  L (1 monolayer  $\sim 37$  L, 1 L =  $1.33 \times 10^{-4}$  Pa).

The observed blue luminescence produced a broad asymmetric peak similar to that found in thorium dioxide<sup>8</sup> and is attributed to F-center excitation. The intensity of this peak should then be sensitive to the concentration of vacancies in the surface oxide layers.

The decrease in luminescence intensity for increasing oxygen exposure can be understood from what is already known about the defect structure of uranium oxides.<sup>2</sup> The intrinsic disorder in uranium dioxide is of the anion Frenkel type, thus substoichiometric oxides have an excess of oxygen vacancies and hyperstoichiometric oxides have an excess of oxygen interstitials. The decrease in luminescence intensity can be correlated to the decrease in the concentration of oxygen vacancies as the oxide goes from an oxygen deficient to an oxygen excess state. If the oxygen exposures were increased to produce  $U_4O_9$ , an increase in the luminescence intensity would be expected since  $U_4O_9$  is also vacancy rich.

This study demonstrates the utility of luminescence techniques for qualitatively monitoring changes in the defect structure of uranium oxides.

#### ACKNOWLEDGMENTS

We thank R. L. Smith for his technical assistance.

#### REFERENCES

1. W. Mayer, Z. Phys. 85 (1933) 278.
2. C. A. Colmenares, Prog. Solid State Chem, in press.
3. B. T. M. Willis, Nature (London) 197 (1963) 755.
4. B. T. M. Willis, Acta Crystallogr. A34 (1978) 88.
5. G. C. Allen and P. A. Tempest, J. Chem. Soc. Dalton Trans. (1982) 2169.
6. C. A. Colmenares, R. H. Howell, R. K. MacCrone and S. R. Shatynski, 9th Int. Cong. Met. Corr., Toronto, Canada (1984).
7. G. C. Allen, P. M. Tucker and J. W. Tyler, J. Phys. Chem. 86 (1982) 224.
8. R. W. Vook, C. A. Colmenares, R. L. Smith and R. G. Gutmacher, J. of Luminescence 27 (1982) 115.
9. W. McLean, C. A. Colmenares, and R. L. Smith, Phys. Rev. B 25 (1982) 8.