Thermoluminescence and Fluorescence in Thoria

P. J. HARVEY AND J. B. HALLETT

Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

Received July 11, 1974

Single crystals of nominally pure thorium dioxide were annealed for 2 hr at 1400°C in an atmosphere of CO. The reduced crystals were excited with uv radiation and the resulting thermoluminescence (TL) measured in the temperature range 20–360°C at a heating rate of 1.5°C sec⁻¹. The complex thermoluminescence profiles were resolved into individual bands with maxima at 219, 246, 271, 297, and 344°C. Measurement of the TL emission spectra indicates the existence of four "electron-hole" recombination centers. The main emission is a sharp-line doublet at 496 and 503 nm.

Ultraviolet excitation also produced visible fluorescence. Two broad bands were observed at 447 and 565 nm giving rise to "blue" and "orange" fluorescence, respectively. A sharp-line spectrum was identified with peaks at 492, 496, and 503 nm. The sharp-line fluorescence spectrum is similar to the main TL recombination center emission spectrum. The spectrum is due to Pr^{3+} ions.

Doping with Ca^{2+} and Y^{3+} greatly reduces both the thermoluminescence and the sharp-line fluorescence. The evidence suggests a model which involves "hole" capture by Pr^{3+} ions during uv excitation and conversion to Pr^{4+}. Subsequent heating liberates trapped electrons which combine with the Pr^{4+} ions producing excited Pr^{3+} ions. These relax to the ground state by emission of characteristic radiation.

1. Introduction

Optical absorbance studies in ThO_2 (*1, 2*) have indicated the presence of a large number of absorbance bands in both nominally "pure" and doped single crystals. Attempts to relate individual bands to impurities were unsuccessful (*2*). Combining absorbance measurements with fluorescence studies (*3*) was successful in establishing the qualitative effects of impurity doping on the optical properties. More quantitative information on the defect nature of ThO_2 was obtained by Rodine and Land (*4, 5*) and Tint (*6*) using thermoluminescence (TL) and EPR techniques.

The present work combines thermoluminescence and fluorescence investigations in an attempt to obtain information on the activator and recombination centers present in ThO_2 and the effects of Ca^{2+} and Y^{3+} doping on these centers.

2. Experimental

(a) Single Crystals

The preparation of ThO_2 single crystals has been described elsewhere (*3*). The crystals were annealed for 2 hr at 1400°C in a Pt boat in an atmosphere of CO. After the anneal the crystals were slowly cooled to room temperature.

(b) Apparatus

The experimental measurements were made in a Perkin–Elmer MPF-3 fluorescence spectrophotometer. The crystals were mounted on a specially designed copper block which could be heated at a controlled rate to 360°C.

(c) Excitation Measurements

The crystals were excited with uv light from a high pressure Xenon arc lamp. The excitation monochromator band width was 10 nm and the excitation wavelength varied in

10 nm intervals from 200–350 nm. To reduce the amount of stray light a uv-D25 filter with a band pass 240–390 nm was inserted between the excitation slits and the crystal. Later measurements were made using a series of interference filters.[1] The excitation spectra were corrected for the variations in light intensity with wavelength. Excitation times were typically of 10 min duration.

(d) Fluorescence Measurements

The fluorescence was measured between 360 and 600 nm in a continuous scan. The spectrofluorimeter automatically corrected the spectra for changes in the 1P28 photomultiplier sensitivity. The emission monochromator was generally set at 10 nm. The fluorescence was measured after every 10 min excitation for a series of excitations ranging from 200 to 350 nm in 10-nm intervals.

(e) Thermoluminescence (TL) Measurements

After each 10 min excitation, the crystal was heated in situ at a rate of $1.5° \text{sec}^{-1}$ from 20 to 360°C. The temperature was recorded by a chromel–alumel thermocouple mounted in the copper block directly behind the crystal. The thermocouple had previously been calibrated by comparing its readings with those of a similar thermocouple imbedded in a standard ThO_2 crystal mounted on the copper block.

The TL emission was measured from 360 to 600 nm in discrete 20 nm stages. The crystal was excited at a fixed wavelength for 10 min. The emission wavelength was set (band pass 20 nm) and the crystal heated. After cooling, the excitation conditions were kept constant and the emission reset 20 nm higher. The TL was again measured. This procedure was repeated until the complete emission range 360–600 nm had been measured for one excitation wavelength. The excitation wavelength was reset and the cycle repeated until measurements had been made at 10 nm intervals from 200 to 350 nm. From these measurements the corrected excitation and emission spectra were calculated. Each complex TL profile of intensity vs temperature

[1] Obtained from Thin Film Products, IR Industries Inc. Waltham, Mass.

was resolved into individual bands using a DuPont 310 Curve Resolver.

3. Results

(a) Thermoluminescence Glow Curve

The TL glow curve is shown for the pure ThO_2 in Fig. 1. The complex profile has been resolved into individual bands with maxima at 219, 246, 271, 297, and 344°C. The effect of Ca^{2+} doping reduces the TL by about a factor 30. The intensity is so low that resolution into individual bands cannot be achieved with any certainty. $ThO_2:Y^{3+}$ shows no measurable TL at all.

(b) Thermoluminescence Emission Spectra

The TL emission spectra are illustrated in Fig. 2. At least four bands are evident at approximately 380, 440, 500 (very large), and 540 nm. The emission is not the same for each TL glow curve band, the lower temperature bands exhibit more short wavelength emission and less 500 nm emission than do the higher temperature bands.

(c) Thermoluminescence Excitation Spectra

The corrected excitation spectra indicate that the lower temperature TL bands have a broad 200–300 nm dependence with a maximum at about 250 nm, whereas the higher
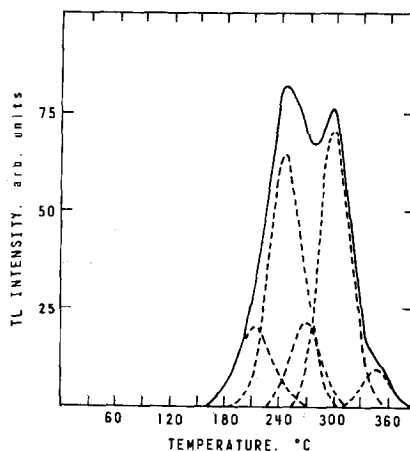

FIG. 1. Thermoluminescence of pure reduced ThO_2 after 10 min excitation with 255 nm light. Emission wavelength 500 nm.
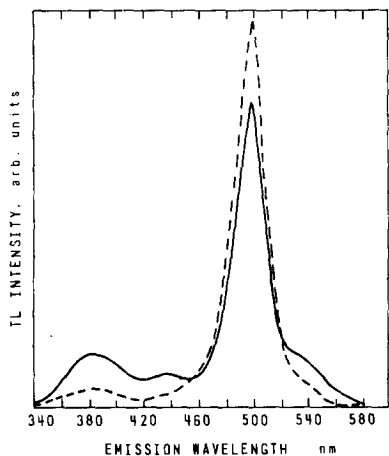
FIG. 2. Emission spectra for the 297 and 246°C TL bands in pure reduced ThO_2 after 255 nm excitation. ---- 297°C Band; ——— 246°C band.

temperature bands have a much narrower wavelength dependence 230–280 nm with a 255 nm maximum.

(d) Fluorescence Emission and Excitation for Pure ThO_2

The emission spectra for pure ThO_2 are illustrated in Fig. 3. The spectrum varies with varying excitation producing a broad band with a maximum at 447 nm for nm excitation, and another broad band at 565 nm maximum with 320 nm excitation. These two bands give rise to the "blue" and "orange" fluorescence, respectively. Also present is evidence for a shoulder at about 520 nm and a sharp-line spectrum in the vicinity of 500 nm. The effect of increasing the excitation intensity and narrowing the emission slits to 2 nm was to resolve the ~500 nm fluorescence into a 496 nm and a 503 nm doublet with a shoulder at 492 nm as shown in Fig. 4. Rapid scanning between 480 and 520 nm during TL emission confirmed that the assymetric 500 nm band had the same 496 and 503 nm doublet.

(e) Fluorescence of $ThO_2:Ca^{2+}$ and $ThO_2:Y^{3+}$ with 278 nm Excitation

The effect of Ca^{2+} and Y^{3+} doping on the sharp-line emission is shown in Fig. 5. The sharp-line spectrum is considerably reduced in the Ca^{2+}-doped ThO_2 and absent in the Y^{3+}-doped crystals.
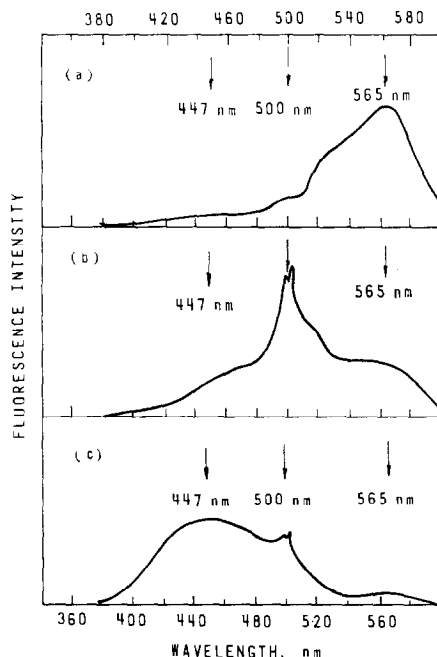

FIG. 3. Fluorescence spectra of pure reduced ThO_2 resulting from (a) 320 nm excitation, (b) 278 nm excitation, and (c) 255 nm excitation.

(f) Time of Excitation

The variation of the fluorescence of pure ThO_2 as a function of time of 255 nm excitation is shown in Fig. 6. As the intensity of the broad 447 nm band increases the intensity of the sharp-line spectrum at 500 nm decreases.
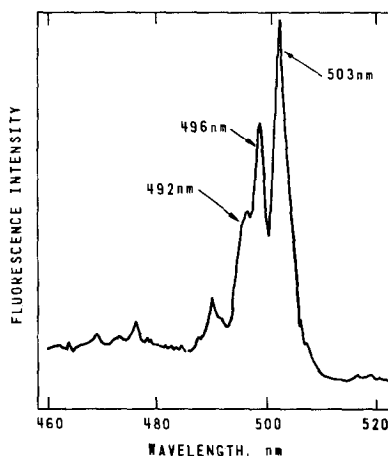

FIG. 4. Fluorescence Spectrum of pure ThO_2 during 278 nm excitation, emission slit 2 nm. Identified as Pr^{3+} impurity.
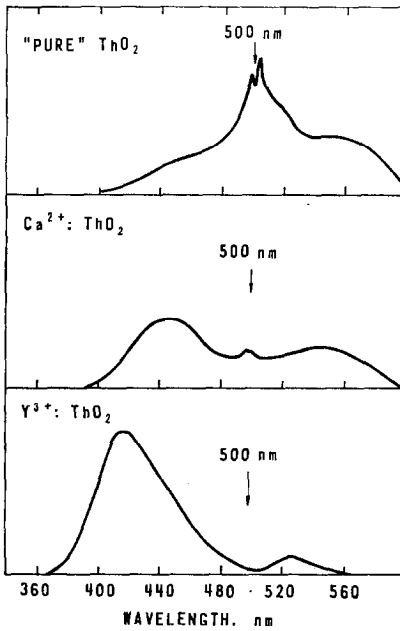
FIG. 5. Fluorescence emission spectra for pure ThO_2, Ca^{2+}:ThO_2 and Y^{3+}:ThO_2 during 278 nm excitation.

4. Discussion

(a) Thermoluminescence

The thermoluminescence results are entirely reproducible provided the conditions are fixed. The annealing temperature atmos-
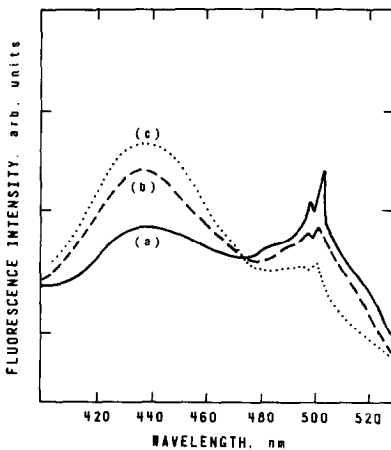

FIG. 6. Effect of excitation time on fluorescence emission spectra of pure ThO_2. (a) 1 min 255 nm excitation; (b) 2 min 255 nm excitation; (c) 10 min 255 nm excitation.

phere, and duration; the rate of cooling after the anneal, the heating rate during TL measurements, must all be strictly controlled in order to obtain a self-consistent set of results.

The glow curve reveals that pure ThO_2 contains at least five trapping sites above 200°C Rodine (4) observed no trapping above 174°C which he suggested was due to exhaustion of recombination sites. Such is not the case in the present work. Kelly and Braünlich (7, 8) have pointed out the pitfalls in attempting to derive trapping energies from glow curves. No attempt has been made in this work to assign any energy values per se.

The emission spectra indicate the presence of four recombination sites, the main site emitting a sharp-line spectrum. The observation that the lower temperature TL glow peaks emit relatively more 380 nm and 430 nm light than the higher temperature peaks suggests that relatively small concentrations of these recombination sites are present in the crystal and that they are exhausted early in the glow curve. If the emission spectrum was the same for each TL band it could be argued that this reflected the trapping probability of each recombination center, but this is not the case.

The main recombination center emits a sharp-line spectrum with peaks at 496 and 503 nm. A sharp-line spectrum is associated with intraconfigurational transitions of the $4f$ shell in trivalent rare-earth ions (9). Various workers (4, 10, 11) have studied the effects of deliberate rare-earth doping and sharp-line spectra for a series of rare-earths have been published. None of the studies gave rise to sharp-line peaks at 496 and 503 nm. However, X-ray excitation optical fluorescence of rare-earths in ThO_2 (12) exhibits a sharp-line spectrum with major peaks at 495.7 and 502.8 nm. This spectrum is unique to trivalent praseodymium. It is, therefore, inferred that the sharp-line emission in the present work is due to decay of Pr^{3+} ions from an excited state to the ground state. Detailed spectral studies of Pr^{3+} (13–17) indicate that optical transitions from the $^3P_0$ and $^3P_1$ to the $^3H_4$ ground state in the $4f^2$ configuration are being observed.

The identification of the main emission as being due to Pr^{3+} suggests that the other

recombination sites may also be rare-earth impurities. While no other sharp-line spectra have been observed it is possible that the small 540 nm emission is due to Er^{3+}, which has a series of sharp-line peaks around this wavelength. Impurity analysis of the ThO_2 lists the major aliovalent impurities as Al 40 ppm, Fe and Ca 20 ppm, Mg 15 ppm, Na, Cl and Ti 10 ppm. Rare-earth concentrations show Gd 5 ppm, La, Ce, and Nd 3 ppm, Pr and Sm 1 ppm, others less than 1 ppm. The analysis of figures for the rare-earths are somewhat surprising and suggest that either the other rare-earths while present in the crystal, may not be incorporated substitutionally in the lattice, or, that the Pr^{3+} impurity ions are closely associated with trapping centers. An additional explanation may be that the Pr^{3+} ions are involved in energy transfer reactions from the other rare-earth ions (18). This area requires additional investigation.

(b) Fluorescence and Impurity Doping

The broad band fluorescence occurring at 447 nm has been discussed in detail elsewhere (3) and the nature and origin of the broad band at 565 nm is still uncertain. The sharp-line-fluorescence, however, is undoubtedly due to Pr^{3+} ions. The effect of Ca^{2+} and Y^{3+} doping is to reduce the sharp-line fluorescence spectrum. Incorporation of Ca^{2+} or Y^{3+} into the ThO_2 lattice and substitutional replacement for Th^{4+} produces a charge unbalance which can be compensated for by the production of oxygen vacancies, the conversion of variable valence impurities to the lower state, or both. These forms of charge compensation should leave the Pr^{3+} concentration either unchanged or increased. The evidence, however, clearly points to a great reduction in the number of free Pr^{3+} ions in the lattice. The reason for this is not known though such effects as complexing, clustering or precipitation may be contemplated. It is, however, this reduction in the number of free Pr^{3+} ions which is responsible for the changes observed in the TL glow curves on doping with Ca^{2+} and Y^{3+}.

The excitation spectrum for the fluorescence of the pure ThO_2 has a maximum at 278 nm giving rise to the sharp-line emission spectrum of the Pr^{3+} ions. The maximum TL, however, is induced by 255 nm light which corresponds to the excitation maximum for the broad 447 nm fluorescence band. Furthermore, during 255 nm excitation the 447 nm fluorescence increases and the sharp-line fluorescence spectrum decreases (Fig. 6). The increase in 447 nm fluorescence is traditionally explained (19) by a model involving the generation of free carriers and their capture by defects in the material. The photokinetic properties of ThO_2 have been detailed elsewhere (20) and enable one to postulate a mechanism to explain the fluorescence and TL behavior of the present material.

(c) Possible Model

In nominally pure ThO_2 near band-gap excitation with uv light at 255 nm produces optical transitions within an activator center or centers which give rise to absorbance and 447 nm broad band fluorescence. A slow build up of fluorescence occurs with time as electrons are thermally raised at room temperature from the excited state of the activator center to the conduction band. Since no optical bleaching is evident the ground state of the activator center must lie in or close to the valence band. Studies in this laboratory indicate that the latter is the more probable. Electrons are thermally excited from the valence band to fill the hole centers created by the optical excitation. Effectively, electrons have been introduced into the conduction band and free holes generated in the valence band. Electrons are trapped at various defect centers and the holes are captured by the Pr^{3+} ions converting them to Pr^{4+}, thereby reducing the fluorescence associated with the trivalent ion. Subsequent heating of the crystal releases the electrons from the trapping centers. The Pr^{4+} ions act as the recombination centers capturing an electron to produce Pr^{3+} in an excited state, which decays to the ground state emitting its characteristic radiation.

References

1. B. G. Childs, P. J. Harvey, and J. B. Hallett, J. Amer. Ceram. Soc. 53, 431 (1970).

2. B. G. Childs, P. J. Harvey and J. B. Hallett, *J. Amer. Ceram. Soc.* **55**, 544 (1972).

3. P. J. Harvey, B. G. Childs, and J. Moerman, *J. Amer. Ceram. Soc.* **56**, 134 (1973).

4. E. T. Rodine, Ph.D. Thesis, University of Nebraska, Lincoln, Nebraska, July 1970. Univ. Microfilms (Ann Arbor, Michigan), Order No. 71-3654.

5. E. T. Rodine and P. L. Land, *Phys. Rev. B* **4**, 2701 (1971).

6. G. S. Tint, Ph.D. Thesis, Temple University, Univ. Microfilms (Ann Arbor, Michigan) Order No. 71-10,588.

7. P. Kelly and P. Braünlich, *Phys. Rev. B* **1**, 1587 (1970).

8. P. Braünlich and P. Kelly, *Phys. Rev. B* **1**, 1596 (1970).

9. G. H. Dieke, "Spectra and Energy Levels of Rare-Earth Ions," (H. M. Crosswhite and H. Crosswhite, Eds.), Wiley, New York, 1968.

10. A. K. Trofimov, *Bull. Acad. Sci. USSR, Phys. Ser.* **25**, 453 (1961).

11. R. C. Linares, *J. Opt. Soc. Amer.* **56**, 1700 (1966).

12. J. R. Saranathan, V. A. Fassel, and E. L. DeKalb, *Anal. Chem.* **42**, 325 (1970).

13. J. Sugar, *J. Opt. Soc. Amer.* **55**, 1058 (1965).

14. R. Sarup and M. H. Crozier, *J. Chem. Phys.* **42**, 371 (1965).

15. H. M. Crosswhite, G. H. Dieke, and W. J. Carter, *J. Chem. Phys.* **43**, 2047 (1965).

16. S. Radhakrishna and B. D. Sharma, *Phys. Rev. B* **9**, 2073 (1974).

17. E. Loh, *Phys. Rev.* **158**, 273 (1967).

18. M. S. Orlov and I. G. Saitkulov, *Bull. Acad. Sci. USSR Phys. Sci* **37**, 1 (1973).

19. S. Shionoya, "Luminescence of Inorganic Solids," (P. Goldberg, Ed.), Academic Press, New York, 1966.

20. P. J. Harvey and J. B. Hallett, *Tech. Report, AECL-4751*, 71 (1974).