

Diffuse reflectance spectra of U ions in ThO₂

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Abstract

Diffuse reflectance spectra obtained at ambient temperature for polycrystalline U_xTh_(1-x)O_{2+y} ceramics fired at 1500 °C in 3.5% H₂/N₂ show several well-defined absorption bands of a 500 cm⁻¹ width in the range of 4000–12 000 cm⁻¹, extending the range of previous measurements. These bands are ascribed to interconfigurational d–d single-ion transitions of U⁴⁺ and increase in intensity with U concentration for $x \leq 0.1$. For higher x values, the intensities of the U⁴⁺ bands peak at $x \sim 0.2$ and then decrease with increasing x to small values only at $x = 1$. Firing in argon at 1500 °C produced enhanced absorption in the 6000–7000 cm⁻¹ range, indicative of U⁵⁺ formation. Further oxidation to U⁵⁺ was produced by firing in air. The detailed shape of the U⁵⁺ peaks depended upon the degree of oxidation and the U/Th ratio. Crown Copyright © 2006 Published by Elsevier B.V. All rights reserved.

1. Introduction

The production of UO₂ nuclear reactor fuel is normally via sintering in a hydrogenous atmosphere. However increased sinterability of UO₂-bearing fuel can be engendered by first sintering in air and then completing the cycle in hydrogen. UO₂-ThO₂ fuels offer increased burnups via the breeding of fissile ²³³U from the Th in addition to the fissile ²³⁵U and there is recent renewed interest in such fuel [1–4]. These fuels can be produced by sintering in air.

It is of interest to explore the valence of the U for UO₂-ThO₂ samples prepared under a variety of atmospheres. For this purpose we have used diffuse

reflectance spectroscopy to examine possible single-ion d–d transitions of U ions and thereby assist in evaluating the valence of the U ions. U⁴⁺ and U⁵⁺ give very different single-ion electronic absorption spectra in suitably dilute samples in the visible and near-infrared regions [5], whereas in X-ray photoelectron or near-edge X-ray absorption, the energy separations of the different U valences are not always large compared to the linewidths. Moreover the very thin (a few nanometer) surface layers traversed in X-ray photoelectron spectroscopy can give problems due to atmospheric surface oxidation effects.

U⁴⁺ gives rise to optical absorption bands of a few 100 cm⁻¹ in width over a large spectral range, whereas U⁵⁺ gives only a few such bands in the vicinity of 6000–10 000 cm⁻¹. Previous work on transmission optical spectroscopy over the red and very near infrared sections of the spectrum for UO₂

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($\sim 13\,000\text{--}17\,000\text{ cm}^{-1}$) has shown the presence of weak absorption bands ascribed variously to U^{4+} ions [6] and excitonic phenomena [7], with the stronger absorption towards the ultraviolet being ascribed to charge transfer between U^{4+} and higher valence states of U [6]. Also, dilution of the U^{4+} into ThO_2 was carried out [6] and the weak U^{4+} absorption bands could be observed further towards the ultraviolet region. Finally, a near infrared absorption band near 1.6 microns (6250 cm^{-1}) was observed in oxidised $\text{U}_{0.301}\text{Th}_{0.699}\text{O}_{2+x}$ and U_3O_8 [8] and attributed to U^{5+} .

2. Experimental

$\text{U}_x\text{Th}_{(1-x)}\text{O}_{2+y}$ samples were prepared from aqueous mixtures of fine ThO_2 powder and uranyl nitrates, followed by stir-drying, calcination in air for 1 h at $750\text{ }^\circ\text{C}$, wet-milling using zirconia balls, pelletising, and firing for 16 h at $1500\text{ }^\circ\text{C}$ in argon in the first instance, followed by firing in air or 3.5% H_2/N_2 at selected temperatures. Some samples were dilute in U to promote single-ion U spectral behaviour and the values of x were 0.001, 0.003, 0.01, 0.03 and 0.1, while more samples richer in U were also studied.

A Philips diffractometer was used for X-ray diffraction, employing Cu $K\alpha$ radiation. All samples fired in 3.5% H_2/N_2 or argon showed only fluorite-type X-ray reflections. Careful lattice parameter measurement or differential thermal analysis in a different atmosphere to try to evaluate the precise oxygen/metal ratio was beyond the scope of this work, and in any case such measurements have been carried out by other workers [8–10].

Scanning electron microscopy (SEM) on polished surfaces of samples was carried out on a JEOL 6400 machine run at 15 kV and fitted with a Tracor Northern TN5502 energy-dispersive spectrometer (EDS) which utilised a comprehensive range of standards for quantitative work. SEM showed the samples to be somewhat porous (see Fig. 1).

Pellet surfaces were coarsely polished with 1200 grit SiC powder to assist diffuse reflectance while some samples had been reduced to powders upon oxidation; spectra were measured on both powders and pellets as appropriate at ambient temperature using a Cary 500 spectrophotometer equipped with a Labsphere Biconical Accessory. Spectra are referenced to that of a Labsphere certified standard (Spectralon), and transformed into Kubelka–Munk units, $F(R) = (1-R)^2/2R$ [11].

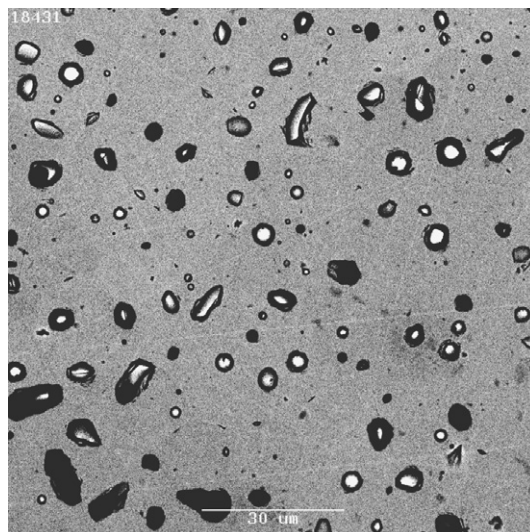


Fig. 1. SEM backscattered micrograph of the $x=1$ sample shows porosity. The white patches in the pores are due to electron reflection and are not due to impurity phases. Micrographs of the other samples were similar.

3. Results

Diffuse reflectance spectra are shown in Figs. 2 [for U contents up to 0.1 formula units(f.u.)] and 3 for samples reduced in 3.5% H_2/N_2 at $1500\text{ }^\circ\text{C}$. All samples were black in color. It is well accepted that U is tetravalent in $(\text{UTh})\text{O}_2$ samples sintered in hydrogenous atmospheres at $\sim 1500\text{ }^\circ\text{C}$ (see above), so zero-phonon d–d transitions of U^{4+} in the eight-fold cubic environment are presumably responsible for the absorption bands having widths of a 500 cm^{-1} . There are no doubt further broader vibronic contributions to the absorption, especially since the dilute substituted U^{4+} ions have inversion symmetry. For the samples containing up to 0.1 f.u. of U, all the peaks increased in intensity with increasing U, except for the narrow peak at 6545 cm^{-1} in the $x=0.001$ and 0.003 samples, though there were somewhat broader peaks centred around this energy in the $x=0.01$, 0.03 and 0.1 samples. The intensities of the sharp absorption peaks began to decrease as x increased beyond 0.1–0.2 and apart from the peaks near $4000\text{--}4500\text{ cm}^{-1}$ were hardly detectable in the sample with $x=1$ (Fig. 3). This behaviour is not unexpected since the spectrum of pure UO_2 has been interpreted on the basis of a collective excitonic picture [7], rather than on a single-ion basis [6], as mentioned previously.

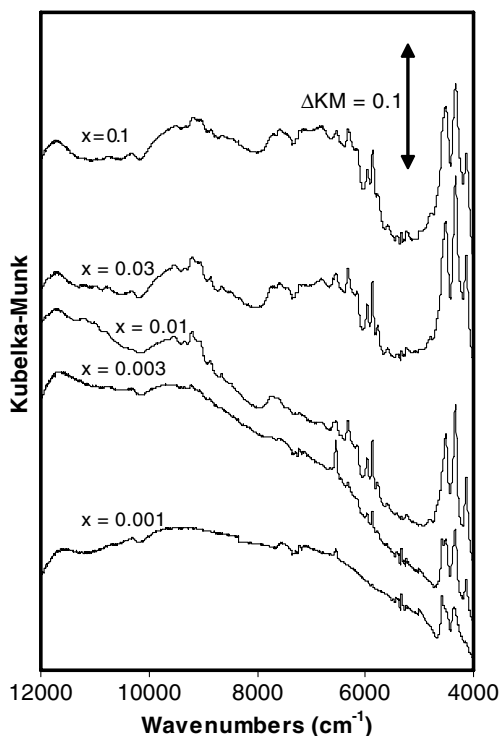


Fig. 2. DR spectra ($4000\text{--}12000\text{ cm}^{-1}$) of $\text{U}_x\text{Th}_{1-x}\text{O}_2$ ($x \leq 0.1$) sintered in H_2/N_2 at $1500\text{ }^\circ\text{C}$.

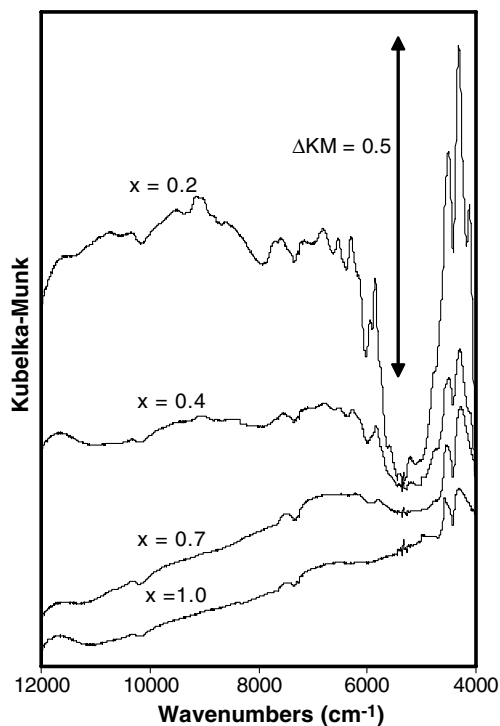


Fig. 3. DR spectra ($4000\text{--}12000\text{ cm}^{-1}$) of $\text{U}_x\text{Th}_{1-x}\text{O}_2$ ($x > 0.1$) sintered in H_2/N_2 at $1500\text{ }^\circ\text{C}$.

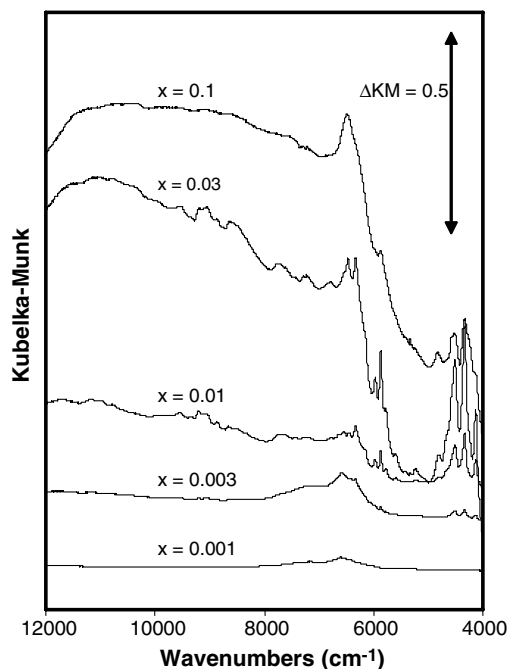


Fig. 4. DR spectra ($4000\text{--}12000\text{ cm}^{-1}$) of $\text{U}_x\text{Th}_{1-x}\text{O}_2$ ($x \leq 0.1$) sintered in argon at $1500\text{ }^\circ\text{C}$.

When the samples containing ≤ 0.1 f.u. of U were heated in argon at $1500\text{ }^\circ\text{C}$ the features attributed to U^{4+} were reduced in intensity and new absorption features in the $6000\text{--}7000\text{ cm}^{-1}$ region were observed (Fig. 4). These would correspond to ${}^2\text{F}_{5/2}\text{--}{}^2\text{F}_{7/2}$ transitions of U^{5+} , as found by Cohen and Berman [8] in oxidised $\text{U}_{0.301}\text{Th}_{0.699}\text{O}_{2+x}$. The new absorption bands only approximately increased in intensity with increasing U content. The new peak(s) near 6500 cm^{-1} was clearly at least duplex with a splitting of $\sim 200\text{ cm}^{-1}$ for the $x = 0.003, 0.01$ and 0.03 samples; however in the more dilute samples it was not possible to accurately distinguish the U^{5+} peaks from the pre-existing U^{4+} peaks.

The DR spectra for $x = 0.2, 0.4$ and 0.7 samples heated at $1500\text{ }^\circ\text{C}$ in air (Fig. 5) also showed a new duplex peak near 6500 cm^{-1} in addition to the U^{4+} peaks near $4000\text{--}4500\text{ cm}^{-1}$. However there are differences in detail between these spectra in the vicinity of 6500 cm^{-1} and those for the oxidised $\text{U}_{0.301}\text{Th}_{0.699}\text{O}_{2+x}$ material [8].

Our UO_2 sample formed U_3O_8 powder on heating in air at $1100\text{ }^\circ\text{C}$ as expected and the diffuse reflectance spectrum of the U_3O_8 is also given in Fig. 6 and we attribute the duplex peak at 6445 and 6655 cm^{-1} to U^{5+} [8]. As in previous work [8], there were hints of a very weak extra band in our U_3O_8 sample near $1.36\text{ }\mu\text{m}$ ($\sim 7350\text{ cm}^{-1}$), but

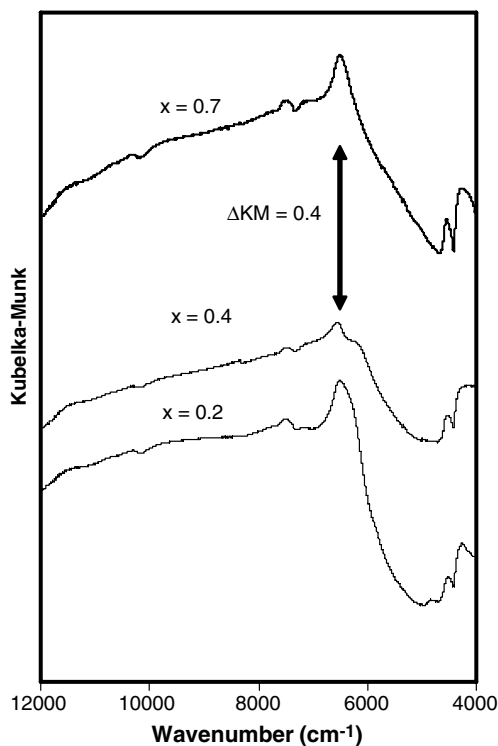


Fig. 5. DR spectra ($4000\text{--}12000\text{ cm}^{-1}$) of $\text{U}_x\text{Th}_{1-x}\text{O}_{2+y}$ ($x = 0.2, 0.4$ and 0.7) heated in air at $1500\text{ }^\circ\text{C}$.

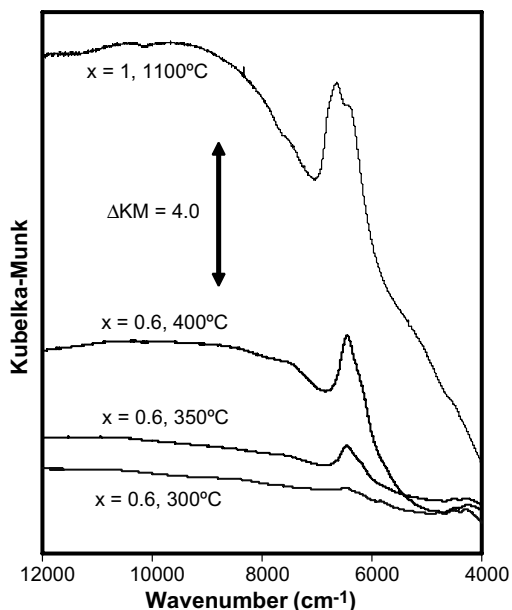


Fig. 6. DR spectra ($4000\text{--}12000\text{ cm}^{-1}$) of $\text{U}_x\text{Th}_{1-x}\text{O}_{2+y}$ ($x = 0.6$) heated in air for 10 h at $300\text{--}400\text{ }^\circ\text{C}$ and of U_3O_8 produced by heating UO_2 in air at $1100\text{ }^\circ\text{C}$.

because U^{6+} has a full shell configuration, this peak would, contrary to the suggestion of [8] and see above, not be due to U^{6+} . The peak (if it exists at all) could easily derive from a second electronic transition within the crystal-field split ${}^2\text{F}_{5/2}\text{--}{}^2\text{F}_{7/2}$ levels of U^{5+} . The detailed variations in peak structure for different U^{5+} -bearing samples could arise from a change of U^{5+} symmetry as the oxidation progresses and the remoteness or otherwise of the charge compensating entities when U^{4+} is oxidised to U^{5+} . Also, the average bond length will change as the U/Th ratio changes.

A sample with $x = 0.6$ was heated in air for 10 h at temperatures in the $300\text{--}400\text{ }^\circ\text{C}$ range and the results are also shown in Fig. 6. Increasing the temperature increased the intensity of the U^{5+} band near 6500 cm^{-1} . The U^{5+} band positions found for the $x = 0.6$ sample are somewhat different to those given by [8] for their $x = 0.301$ sample and the peaks at near 6500 cm^{-1} are narrower than those of U_3O_8 due to the greater apparent band splitting in the case of U_3O_8 .

4. Conclusion

Diffuse reflectance spectroscopy confirms that all the U is tetravalent in $(\text{UTh})\text{O}_2$, with more data being obtained in the near infrared than in a previous investigation [6], and the intensities of the bands increase with increasing x for $x \leq 0.1$. The single-ion character of the spectra is progressively lost as the U content of the samples is increased. Substantial amounts of the U in dilute samples heated in argon at $1500\text{ }^\circ\text{C}$ are present as U^{5+} . U_3O_8 produced by heating UO_2 in air at $1100\text{ }^\circ\text{C}$ also showed a duplex diffuse peak near 6500 cm^{-1} , again attributable to U^{5+} .

Acknowledgements

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