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Diffuse reflectance spectroscopy of tetravalent neptunium and plutonium ions in ThO_2

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Abstract

Near infrared (4000–12 000 cm^{-1}) absorption spectra of Pu^{4+} and Np^{4+} dilutely incorporated in air-fired polycrystalline ThO_2 were collected at ambient temperature and showed several well-defined absorption bands having widths of a few hundred cm^{-1}. These bands are ascribed to f–f single-ion electronic transitions and increase in intensity with Np and Pu concentration up to 0.03 formula units (f.u.). Reheating samples in H_2/N_2 atmosphere at 1400 °C did not produce obvious spectral change for Np-doped ThO_2 and therefore no evidence of the formation of Np^{3+}. However, the spectral lines attributed to Pu^{4+} decreased by approximately a factor of six in intensity, which implies reduction of Pu^{4+} to Pu^{3+}.

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1. Introduction

The first aqueous absorption spectrum of the tetravalent neptunium [Np^{4+} ($5f^3$)] was obtained 50 years ago [1]. However, the optical spectroscopy of Np^{4+} in the solid state has been studied in only a few crystalline matrices [2]. Because of the high density of states (overlapping of the excited crystal-field levels as the photon energy increases) as a result of larger spin-orbit coupling combined with larger crystal-field interactions, compared to its lanthanide analogue Nd^{3+} ($4f^3$), only the Stark components of the four lowest manifolds, $^4I_{9/2}$, $^4I_{11/2}$, $^4F_{3/2}$ and $^4I_{13/2}$, which are well-isolated, can be reasonably assigned and fitted for parametric analysis in condensed media [2]. Electronic spectra of Np^{4+} in D_{2d} symmetry, in $ThSiO_4$ [3], $PbMoO_4$ [4] and $ZrSiO_4$ [5] have been investigated. Also, optical data have been published for Np^{4+} in octahedral and cubic crystal fields, $CsNpCl_6$ [6], $[(C_2H_5)_4N]_2NpCl_6$ [7], NpF_4 [8] and ThO_2 [9,10] where Np^{4+} ions occupy a site of inversion symmetry in each case. It has been argued for Np^{4+} in ThO_2 that a small distortion has lifted the inversion symmetry at the Np^{4+} site sufficiently to permit the observation of forced (zero-phonon) electric dipole transitions in the optical region [9]. However, recent work [10] has shown the vibronic character of the spectra (as expected if inversion symmetry has been maintained), in contradiction with the previous work [9], and also proposed the existence of Np^{3+} to explain absorption bands seen at around 7200 cm^{-1}. Note however if Np^{3+} was present, a spectrum similar to that of iso-electronic Pu^{4+} would be expected, contrary to observation.

Although the aqueous absorption spectrum of the tetravalent plutonium [Pu^{4+} ($5f^4$)] was reported [11] at about the same time as its neptunium counterpart, the optical spectroscopy of Pu^{4+} in the solid state has been reported so far only in tetrafluoride [8] and $ThSiO_4$ matrices [3].

Crystalline Th^{4+} compounds have often been used to study optical spectroscopy of paramagnetic actinide ions [10], mainly because Th^{4+} has no 5f electron, making it possible to observe f–f electronic transitions of other actinide ions incorporated in solid solution. In addition, Th^{4+} has a similar ionic radius as other actinide ions so it can be substituted by other actinide ions without much site distortion [11], especially if the substituted actinide ion is tetravalent.

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In the literature, little theoretical modelling of Np^{4+} and Pu^{4+} spectra in the condensed phase with well-defined symmetry character has been attempted [12]. The complexity of Np^{4+} and Pu^{4+} spectra arising from transitions within partly filled 5f shells is mainly due to the fact that there is a large number of free-ion states which lie close to one another and which are further split by crystal fields which have the same order of magnitude as the inter-electronic repulsion and the spin-orbit coupling [13]. In addition, different splitting patterns and transition intensities arising from different site-symmetries and selection rules are probably only detectable for zero-phonon transitions in low temperature spectra.

The ThO_2 structure is isomorphic to CaF_2 with O_h space group symmetry and the Th ion sits at the centre of an eightfold cube with inversion symmetry [9]. Recently we have studied uranium valences in ThO_2 sintered under different atmospheres [14]. It is of interest for both advanced nuclear fuels and high-level radioactive waste forms to understand Np and Pu valences in oxides, noting that the actinide valence depends on crystal-chemical forces as well as the oxygen fugacity. For these purposes, in the current work we have used diffuse reflectance spectroscopy to study f–f electronic transitions of Np and Pu ions in ThO_2 to assist in evaluating the valence of Np and Pu in other oxide ceramic fuels.

2. Experimental

$(Np/Pu)_xTh_{1-x}O_2$. samples were made by the standard oxide/nitrate route (from mixtures of fine ThO_2 powder and Np/Pu nitrate solutions), followed by stir-drying, calcination in air for 1 h at 750 °C, wet-milling using zirconia balls, pelletising, and firing for 16 h at 1500 °C in air. Samples were mostly dilute in Np/Pu with x ranging from 0.001 to 0.1 to promote single-ion spectral behaviour. End member NpO_2 and PuO_2 samples were also prepared. Some samples were reheated in 3% H_2/N_2 at 1400 °C for 16 h to see whether trivalent Np/Pu ions can be stabilised in ThO_2 as proposed by previous workers [10] who studied Np-doped ThO_2 single crystals.

A Philips diffractometer was used for X-ray diffraction, employing Cu Kα radiation. All samples fired in air or 3% H_2/N_2 showed only fluorite-type X-ray reflections. 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 all samples to be single phase and somewhat porous (see Fig. 1).

Pellet surfaces were coarsely polished using SiC paper up to 9.5 μm finish to assist diffuse reflectance. Diffuse reflectance (DR) spectra were collected on pellets at ambient temperature using a Cary 500 spectrophotometer equipped with a Labsphere Biconical Accessory. Spectra are referenced to that of a Labsphere certified standard

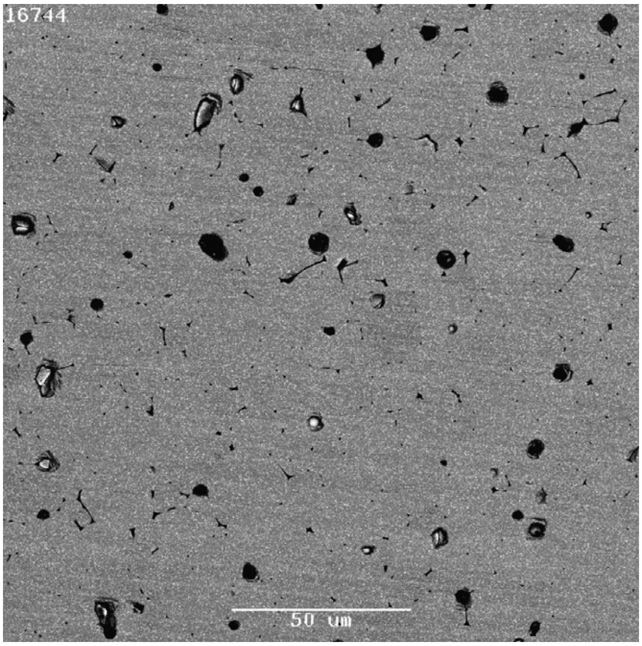

Fig. 1. SEM backscattered micrograph of the polished $Pu_{0.1}Th_{0.9}O_2$ sample shows it is single phase but porous. The white patches in the pores are due to electron reflection and are not impurity phases. Micrographs of the other samples were similar.

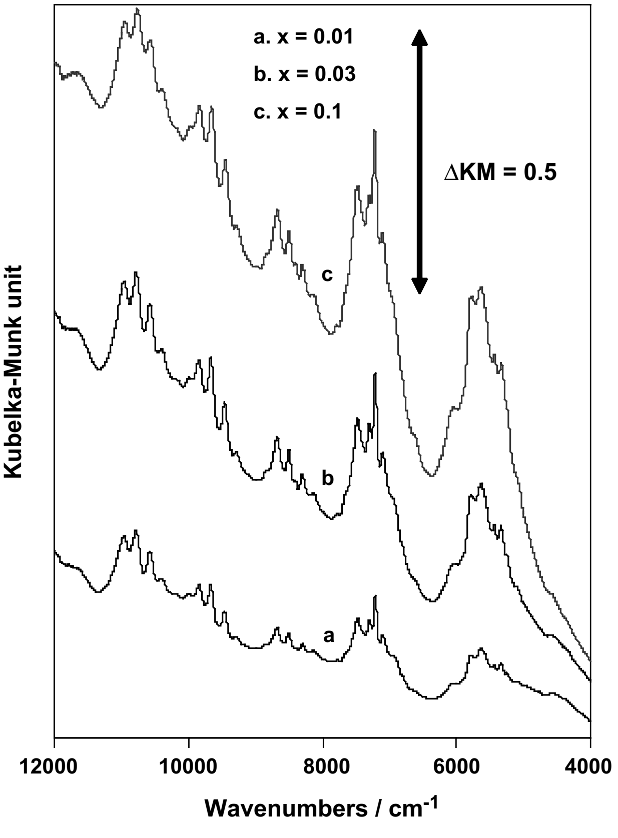

Fig. 2. DR spectra (4000–12000 cm^{-1}) of $Np_xTh_{1-x}O_2$ ($x = 0.01$, 0.03 and 0.1) samples sintered in air at 1500 °C.

(Spectralon), and transformed into Kubelka–Munk units, $F(R) = (1-R)^2/2R$ [15].

3. Results

3.1. Absorption spectra of Np^{4+} in ThO_2

DR spectra in the near infrared range for Np contents up to 0.1 f.u. in ThO_2 are shown in Fig. 2. It is well accepted that Np is tetravalent in $Np_xTh_{1-x}O_2$ samples sintered in air. Therefore f–f transitions of Np^{4+} in the eightfold cubic environment are presumably responsible for the absorption bands having widths of a few hundred cm^{-1}. There are no doubt further broader vibronic contributions to the absorption, especially since the dilutely substituted Np^{4+} ions would be expected to have inversion symmetry. Our spectra at room temperature agree broadly with those in Ref. [10], although ours are broader due to the higher sample temperature. Apart from absorption bands at around 7200 cm^{-1} (see above), most absorption bands are fairly consistent with those reported in single crystals of Np^{4+}:ThO_2 [9,10], with different groups of bands corresponding to J states $^4I_{11/2}$ at ~5600 cm^{-1}, $^4F_{3/2}$ at ~8700 cm^{-1}, $^4I_{13/2}$ at ~9900 cm^{-1} and $^4F_{5/2}$ at ~11 000 cm^{-1}. Ref. [9] assigned all observed transition bands (other than the band at 7200 cm^{-1}) to well-defined spin-orbit groups. However, it did not show any of the measured spectra. Although Ref. [10] anticipated the existence of Np^{3+} in ThO_2 due to the additional bands observed at around 7200 cm^{-1}, we provide an alternative possible explanation below (and see above).

There is no evidence of additional peaks with increasing Np up to 0.1 f.u. and in general, most absorption peaks increase in intensity with increase of Np content up to 0.1 f.u. as expected by Kubelka–Munk theory [15]. The DR spectrum for NpO_2 sintered in air at 1500 °C is shown in Fig. 3. As for UO_2 [14] in which most of the single-ion f–f electronic transitions of U^{4+} are hardly detectable due to collective excitonic phenomena [16], single-ion f–f electronic transitions in NpO_2 were not detectable.

To bear on the question of possible presence of Np^{3+} in ThO_2 (see above), a sample with 0.1 f.u. of Np in ThO_2 was reheated in 3% H_2/N_2 at 1400 °C for 16 h to try to reduce Np^{4+} to Np^{3+} and the DR spectrum is shown in Fig. 4 compared to the one before reheating. The sample remained dark brown in color in both oxidised and reduced conditions. The reduction process made no obvious change to the broad absorption bands around 7200 cm^{-1} and did not increase absorption at around 4000 cm^{-1} ($^5I_5$), suggesting that the broad absorption bands at around 7200 cm^{-1} are most likely to be the result from vibronic contributions from Np^{4+} [17] rather than from Np^{3+} ($^5I_6$) as proposed by

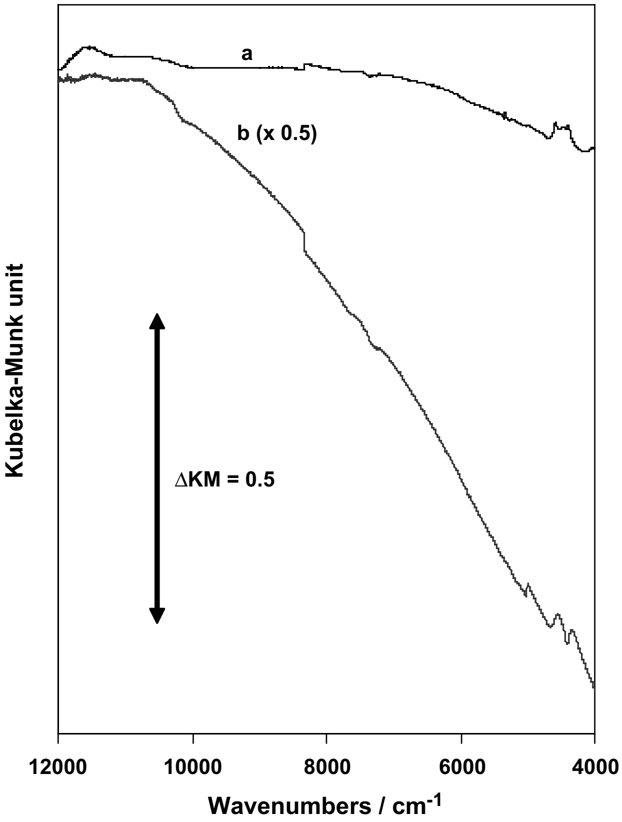

Fig. 3. DR spectra (4000–12 000 cm^{-1}) of (a) NpO_2 and (b) PuO_2 (dilutely incorporated in TiO_2 powder) sintered in air at 1500 °C (spectra offset vertically to enhance visibility).

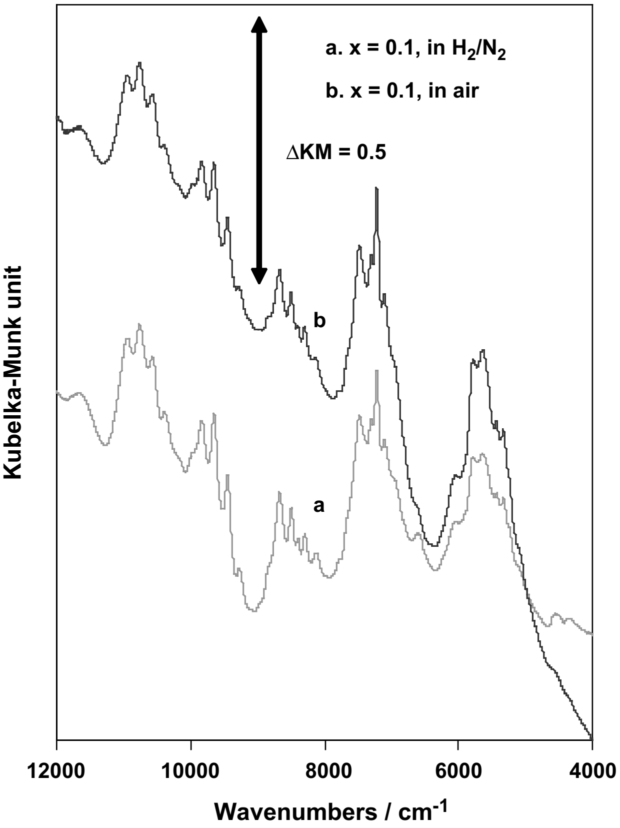

Fig. 4. DR spectra (4000–12 000 cm^{-1}) of $Np_{0.1}Th_{0.9}O_2$ samples (a) reheated in 3% H_2/N_2 at 1400 °C for 16 h, (b) sintered in air (spectra offset vertically to enhance visibility).

other workers [10]. This means that it is an oversimplification to assign the spectra simply to lines of well-defined spin-orbit groups, and that mixing of the various basis states needs to be factored into any rigorous parametric analysis.

3.2. Absorption spectra of Pu in ThO_2

DR spectra, in the near infrared range, for Pu contents up to 0.1 f.u. in ThO_2 are shown in Fig. 5. It would be expected that substitutional Pu in air-fired ThO_2 would be tetravalent [18]. Therefore, the spectra in Fig. 5 are attributable to f–f electronic transitions of tetravalent Pu ions in ThO_2. Most of the absorption peaks increased with increase of Pu content up to 0.03 f.u. (i.e. Kubelka–Munk theory is roughly valid) and remained relatively constant with Pu contents from 0.03 to 0.1 f.u. Like UO_2 [14] and NpO_2 (see above), the DR spectrum of PuO_2 (shown in Fig. 3, note the PuO_2 sample is diluted into TiO_2 which has a strong background absorption dependence on photon energy) has no detectable f–f electronic transitions in the near-infrared range due to the loss of single-ion behaviour [16].

A sample containing 0.03 f.u. of Pu was reheated in 3% H_2/N_2 at 1400 °C for 16 h and the DR spectrum in the near-infrared range is shown in Fig. 6, together with the one without reheating. The sample changed in color from light brownish to dark brown after reheating in the reducing atmosphere. The reduced sample gives a very similar spectrum except for a slightly elevated absorption at ~4500 cm^{-1} and overall weaker absorption intensities (4–8 times weaker). A few oxidation–reduction cycles confirmed that the observed phenomena are reversible, showing that the effect is not due to volatilisation losses of Pu. However, it is difficult to resist the idea that the decrease of the intensities of the absorption peaks due to Pu^{4+} must show the formation of a different Pu valence state, notably Pu^{3+}. Pu^{3+} ($5f^5$) would be expected to give rise to a considerably higher density of transition in photon energy space than Pu^{4+} and it may be that this is the reason why peaks due to Pu^{3+} could not be clearly observed, especially as Pu^{3+} would likely have inversion symmetry so that only electron dipole allowed vibronic transitions would be possible (neglecting very weak magnetic dipole transitions). It is relevant that diffuse reflectance peaks due to Pu^{3+} in $CaTiO_3$ could not be clearly observed [19].

To further explore the reason of weaker absorption intensities upon reduction, DR spectra of the above two samples, in the UV-visible range, were also collected (shown in Fig. 7). The two spectra are similar in the UV-visible range except for slightly elevated absorption at ~21 600 cm^{-1} for the reduced sample.

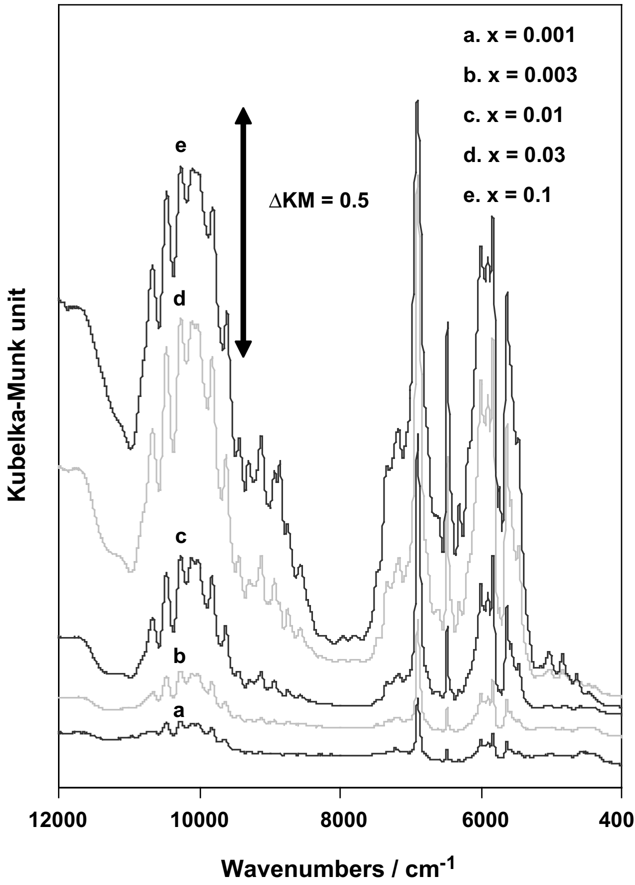

Fig. 5. DR spectra (4000–12000 cm^{-1}) of $Pu_xTh_{1-x}O_2$ ($x = 0.001$ to 0.1) samples sintered in air at 1500 °C (spectra offset vertically to enhance visibility).

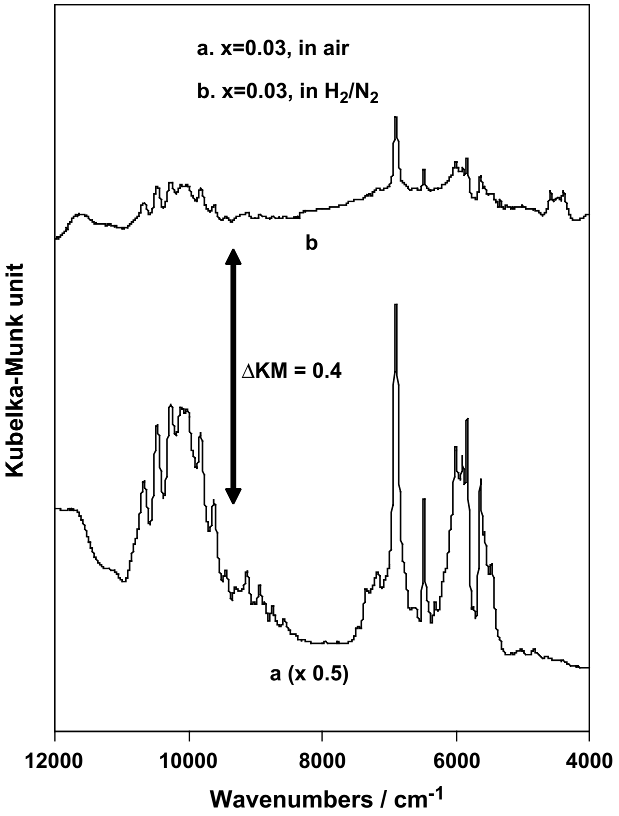

Fig. 6. DR spectra (4000–12000 cm^{-1}) of $Pu_{0.03}Th_{0.97}O_2$ sample, (a) sintered in air, (b) reheated in 3% H_2/N_2 at 1400 °C for 16 h.

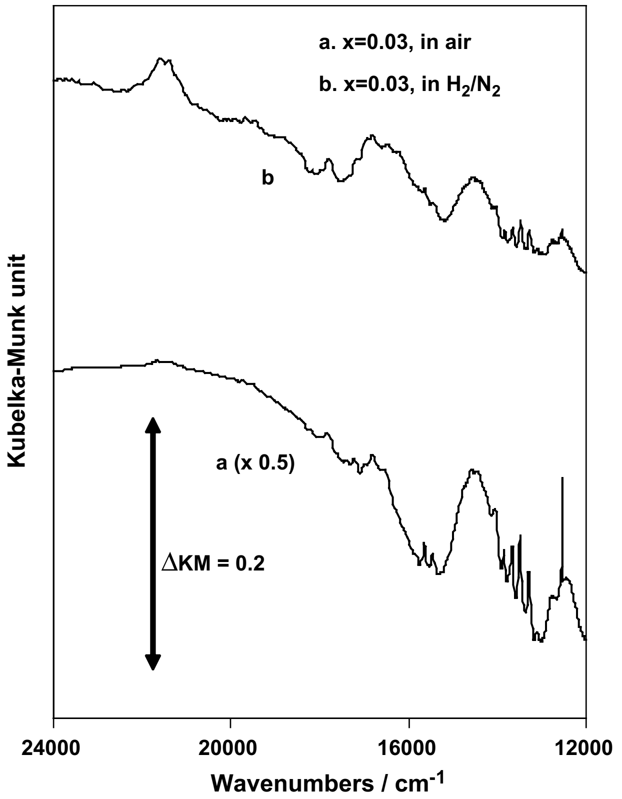

Fig. 7. DR spectra (12000–24000 cm^{-1}) of $Pu_{0.03}Th_{0.97}O_2$ sample, (a) sintered in air, (b) reheated in 3% H_2/N_2 at 1400 °C for 16 h.

4. Conclusion

We have confirmed by using diffuse reflectance spectroscopy that both Np and Pu exist as tetravalent ions in diluted $(Np/Pu)_xTh_{1-x}O_2$ solid solutions fired in air, and the intensities of the f–f electronic transitions increase with increasing x to $x \leqslant 0.03$. The f–f electronic transitions show no single-ion features when $x = 1$. There is no evidence of trivalent Np ions in the samples after being reheated in strongly reducing atmospheres, but there is indirect evidence of Pu^{3+} on such reheating.

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