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The Debye Temperature for Hydrothermally Grown ThO₂ Single Crystals

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ABSTRACT

The electronic properties of ThO₂ single crystals were studied using x-ray photoemission spectroscopy (XPS). The XPS results show that the Th 4*f* core level is in an oxidation state that is consistent with that expected for Th in ThO₂. The effective Debye temperature is estimated from the temperature dependent photoemission intensities of the Th 4*f* core level over the temperature range of 290 to 360 K. A Debye temperature of 468±32 K has been determined.

INTRODUCTION

Actinides and their oxides are important for the nuclear fuel cycle and other new energy sources [1]. In particular, there is growing interest in a thorium fuel cycle due to thorium's natural abundance, refractory nature, and potentially limited radioactive waste formation [2]. While refractory suggests high temperature stability, a low Debye temperature translates into low barriers to surface and grain boundary segregation of impurities, as well as a possible propensity for phase separation, as in the case of Gd-Ni [3]. A medium Debye temperature, say in the region of 600 K or more, generally implies that surface segregation must be thermally activated, or that significant radiation damage and vacancy creation must occur prior to facile surface and grain boundary segregation of impurities.

While the technique of hydrothermal crystal growth is not new, hydrothermally grown single crystals of ThO₂ are an excellent route for obtaining large single crystals of actinide oxides, sufficient for an accurate determination of the effective Debye temperature as well as possible differences in the surface and the bulk Debye temperatures [4]. The XPS determined Debye temperature is also useful in elemental "specific" studies in order to help ascertain if dopants occupying similar sites within a host matrix form similar types of bonds [5]. Additionally, the changes in the effective Debye temperature are a useful signature in quantifying and identifying phonon mediated transitions [6] from temperature dependent photoemission studies [7].

The investigations here are aimed at addressing whether ThO₂ is robust as a single crystal, especially with regard to impurity and vacancy diffusion, in spite of prior measurements that suggest that the Debye temperature of ThO₂ is in fact quite low, in the region of 259 to 290 K [8].

EXPERIMENT

ThO₂ single crystals were prepared by the hydrothermal technique in supercritical cesium fluoride mineralizer solutions. Due to the corrosive nature of the mineralizer solution, the reaction was performed in a sealed silver ampoule (Stern Leach, 99.99%) with an inner diameter of 3/8" and an overall length of 8". Thorium oxide (Strem, 99.99%) powder weighing 1.3 g and 4 mL of 6 M CsF (Alfa Aesar, 99.99%) were added to the silver ampoule, which was then welded shut. The ampoule was placed in a 27 mL Inconel autoclave with excess water added to the remaining volume of the vessel. This excess water acts as counter pressure to prevent the ampoule from rupturing during the growth cycle. Once the autoclave was sealed, two band heaters were applied with a top and bottom temperature of 690 and 750° C respectively. The result is 20 kpsi of pressure on the ampoule. The applied conditions were sufficient to spontaneously nucleate single crystals of ThO₂ from a supersaturated mineralizer solution. Crystal formation occurred over an 11 day growth period, at which time the autoclave was allowed to cool to room temperature. The silver ampoule was retrieved from the autoclave and the contents flushed onto filter paper with deionized water. Further growth information is detailed in [9].

The XPS was conducted under ultra high vacuum ($\sim 10^{-10}$ Torr) using an aluminum anode with a K α of 1.486 keV. All the photoemission spectra reported here were taken with this photon energy, with the photoelectron energy distribution curves measured using a hemispherical electron energy analyzer from Thermo VG Scientific, model VG 100 with a pass energy of 100 eV in 0.1 eV steps. The Th 4*f* core level binding energies are references to the Fermi level or chemical potential, calibrated using a Au foil. The temperature was monitored using a type K thermocouple and cross-checked using an infrared pyrometer.

DISCUSSION

Core level binding energies and valancy

The Th 4*f* core level binding energies taken at a temperature of 294±2 K are plotted in Figure 1a. Both core level 4*f* spin-orbit component core level features are readily apparent with binding energies of 337.2 eV (4*f*_{7/2}) and 346.4 eV (4*f*_{5/2}). The intensity ratio of 4*f*_{5/2} to 4*f*_{7/2} is 0.76, close to the expected 0.75 for the angular momentum degeneracy. The metallic Th 4*f*_{7/2} binding energy ranges from 333.1 eV [10-12] to 333.8 eV [13]. The shift of the Th core level peak into a higher binding energy, compared to provide evidence of an oxidize Th, is as expected: the previously reported value of the 4*f*_{7/2} binding energy for ThO₂ is 337.70 eV [14], close to our measured value, although some values for the 4*f*_{7/2} binding energy for ThO₂ are somewhat smaller [15-16].

Additionally, there is a shake-up satellite peak at a binding energy of approximately 353.4 eV. Satellite features are well known [7,15-17] and a shake-up satellite of about 7 eV is consistent with a band gap of about 6 eV for this oxide [17]. The presence of the satellite feature implies that there is the possibility of more than one final electronic state for the XPS process [7,15,17]. In this case, if one assumes a metal-ligand picture, then the main line would occur due to a charge transfer from the O ligands, while the satellite peak results from a final state much like the initial state. This is the view approached by Allen et al. [15] for studies on

various thorium binary compounds, with some variability due to changes in crystal symmetry for the various compounds studied in their work.

Effective Debye Temperature

In fact the Debye temperature must be significant because (Figure 1) the diminution of the XPS intensities with temperature is quite slight. In Figure 1a, the intensity of the lowest temperature (blue) is plotted with the intensity of the highest temperature (red). In order to magnify the difference, a smoothed-difference between the two spectra is plotted in Figure 1b. After background subtraction, as in Figure 1, the relative core level intensities have been plotted in Figure 2. The intensities, relative to the $4f_{7/2}$ intensity at 294.1 K, have been plotted in Figure 2. The errors in the relative intensities are propagated errors, largely dominated by counting statistics, while errors in the temperature will be largely systematic. A linear background has been removed from the intensities before the natural logarithmic ratio is determined.

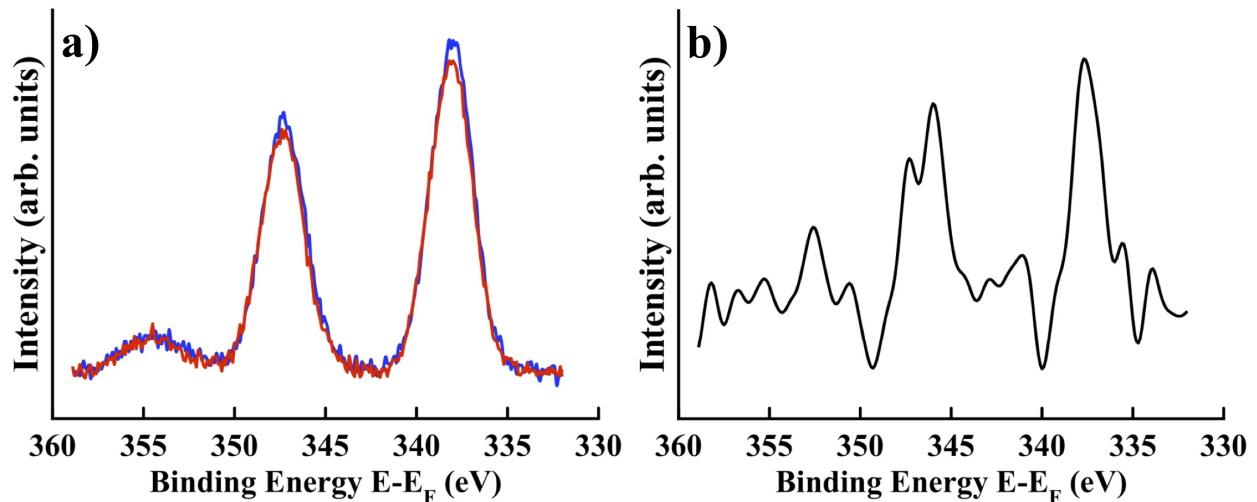


Figure 1: a) XPS of the Th $4f$ levels at 294 (blue) and 354 K (red). b) The difference between the two spectra in a). This difference has been smoothed to more accurately show the peaks. The binding energies of each peak in the figures are at 337.2 eV ($4f_{7/2}$), 346.4 eV ($4f_{5/2}$) and 353.4 (satellite).

The observed decrease in intensity with increasing temperature is generally attributed to an increase in the atomic vibrational motion normal to the sample surface and represented by the Debye-Waller factor W (Equation 1). By measuring the natural logarithmic ratio of intensity as a function of temperature, the slope can be determined and the effective Debye temperature extracted as has been done in many papers and texts previously [4,5,7,18]. In fact we can extract a Debye temperature from the photoemission intensity as:

$$I = I_0 \exp(-2W)$$

$$2W = \frac{3\hbar^2 T (\Delta k)^2}{2mk_B \Theta_D^2} \quad (1)$$

where W is the Debye-Waller factor, T is the temperature of the sample (in Kelvin), $\hbar \Delta k$ is the electron momentum transfer, m is the mass of the scattering center, k_B is the Boltzman constant, and Θ_D is the Debye temperature.

The results of our experimental determination of the effective Debye temperature are tabulated in Table I. There is a slightly different Debye temperature determined for the $4f_{5/2}$ compared to $4f_{7/2}$, though this is primarily attributed to a small overlap between the Gaussian peaks used to fit the $4f_{5/2}$ and satellite peaks. The present conclusion is that the two Debye temperatures are essentially in agreement, with more confidence arising from the values obtained from $4f_{7/2}$ core level intensities due to the greater coefficient of determination (R^2) in Table I. The two Debye temperatures can be considered in agreement with much more confidence in the values attributed for the $4f_{7/2}$ peak. This is, of course, the thorium weighted effective Debye temperature and does not include a strong weight from the oxygen ligand nor does this value include anharmonic contributions.

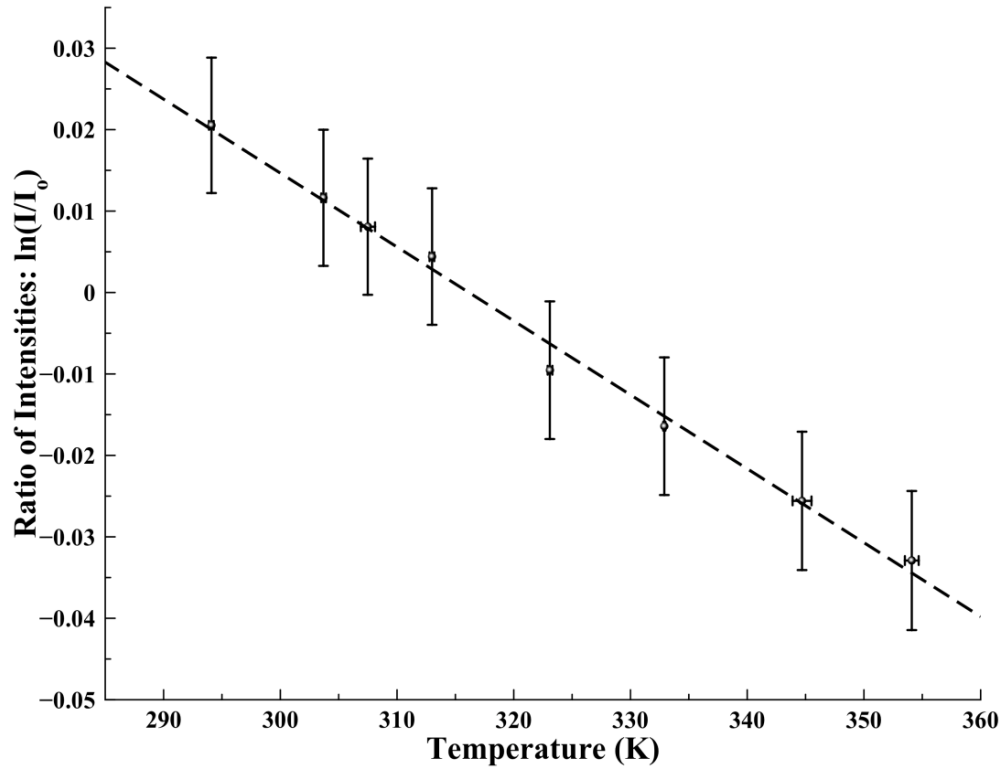


Figure 2: The natural logarithmic ratio of intensities for the $4f_{7/2}$ peak as a function temperature. A linear background was subtracted. The reference intensity I_0 is the intensity for the first measurement made at 294.1 K.

A lower Debye temperature for the satellite peak is more in line with the thermal Debye temperature associated with heat capacity [8], but in fact our value here is in agreement with a recent density functional theory (DFT) calculation using the LDA+U methodology [19] where a Debye temperature of 402.6 K for the ThO₂ fluorite structure was estimated. In fact, our data tends to suggest that overall, for good single crystals the Debye temperature is in fact significant.

Table I: The fitting results for the two core 4*f* level and satellite peaks. Any values given in parentheses are standard deviations and provided to ascertain parameter uncertainty.

	Debye-Waller factor W	Δk (\AA^{-1})	Debye temp Θ_D (K)	Fit R^2
4 <i>f</i> _{7/2}	0.0009 (0.00003)	17.1	468 (8)	0.9906
4 <i>f</i> _{5/2}	0.0008 (0.0001)	17.1	502 (34)	0.8209
satellite	0.0045 (0.0005)	17.0	205 (12)	0.9642

CONCLUSIONS

The Th 4*f* core level binding energies and effective Debye temperature have been investigated using temperature dependent x-ray photoemission spectroscopy. Two Th 4*f* peaks are observed with binding energies that are in good agreement with the values expected for ThO₂ and accompanied by a satellite feature consistent with a shake-up. The experimentally determined Debye temperature is 468±32 K but is a value strongly weighted for thorium alone. Nonetheless, the results determined experimentally here are in good agreement with the results of a recent DFT calculation (402.6 K) for the ThO₂ fluorite structure.

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