The low-temperature heat capacity of the (Th,Pu)O₂ solid solution

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1. Introduction

In the context of evaluating the prospects of thorium-based fuel for generation IV nuclear reactors [1], a substantial effort is made in studying the thermal properties of its mixed oxides with the actinide elements uranium and plutonium. Numerous investigations were performed in a wide temperature range to understand the behaviour of this potential nuclear fuel from thermodynamic point of view [2–9].

Heat capacity is one of the key thermodynamic properties as it describes the relation between the heat change and temperature of a material. It also reveals essential information about phase transitions, lattice vibrations, energy excitations and defect structures of a material. It is clear that for any material the heat capacity tends to decrease strongly with decreasing temperature, finally reaching zero at the absolute zero temperature in case of a perfect crystal. When a mixed oxide solid solution is considered, the heat capacity is strongly related to the end-members. However, the substitution of iso-valent ions with different sizes on the cation sublattice is changing the interatomic distances of the first nearest neighbour atoms by compression or expansion of the bonds. Also contributions to the heat capacity that are of electronic origin, such as Schottky anomalies, may be affected by the dilution. Therefore the behaviour of solid-solution materials may deviate from the trend suggested by the end members and may show substantial excess contributions.

In one of our previous studies [10] the heat capacity of thorium–plutonium mixed oxides was investigated in the high-temperature range (476–1790 K). In the present work we have extended our investigations of this system to the low-temperature regime. We have measured the heat capacity of (Th,Pu)O₂ solid solutions with 3, 8, 30, 54 and 85 wt% PuO₂ in the temperature range from a minimum of 3.6 K to about 300 K. This minimum temperature was higher than normally achievable one by the equipment used, due to effects of self-heating resulting from the 239Pu isotope used in our work. Since the literature data for PuO₂ refer to a material containing the 242Pu isotope [11], in which the self-heating is about 15 times lower, we also investigated the 239PuO₂ end-member in the temperature range of 5.9 K up to about 300 K. The complete data set allows a detailed analysis of the variation of the heat capacity for these solid solutions as a function of the composition.

2. Experimental

2.1. Sample preparation

The heat capacity measurements performed in this study were done on samples with different PuO₂ concentrations which were produced by the sol–gel technique. For this process the thorium nitrate and plutonium dioxide were used as starting materials. The preparation and characterisation of the (Th₁₋yPuₙ)O₂ solid
solutions with \( y = 0.03, 0.08, 0.30, 0.54 \) and 0.85 is described in detail in our previous work [10] but also by Cozzo et al. [9]. The pure PuO\(_2\) sample was a fragment of a pellet made from stock material [9,10]. In order to avoid build up of radiation damage, our samples were annealed before the measurement. The isotopic composition of the plutonium used was 91.5\% 239Pu, 8.302\% 240Pu, and 0.685\% 241Am as decay product of 244Pu.

2.2. The PPMS technique

The low temperature heat capacity measurements were performed using a PPMS-9 instrument (Physical Property Measurement System, Quantum Design) in the temperature range 7.3–291.9 K, 3.6–272.2 K, 6.5–291.9 K, 7.3–297.4 K and 8.1–296.6 K for the solid solutions with 3, 8, 30, 54 and 85 wt.% PuO\(_2\) respectively and from 5.9 K to 270.5 K for PuO\(_2\). The instrument installed in our laboratories can determine the specific heat of samples with a relatively small mass (few mg) by a hybrid adiabatic relaxation method. The description of the technique and details of our apparatus and the method of handling radioactive actinide samples can be found in the work of Javorský et al. [13]. The measurements of Th0.97Pu0.03O\(_2\), Th0.92Pu0.08O\(_2\), Th0.70Pu0.30O\(_2\), Th0.46Pu0.54O\(_2\), Th0.15Pu0.85O\(_2\) and PuO\(_2\) were made on small pieces of discs which were wrapped in an appropriate amount of Stycast (2850 FT) low-temperature conductive epoxy. Self-heating correction was taken into consideration and the heat capacity of the corresponding Stycast was measured separately and subtracted, resulting in an uncertainty of the measurements of 3–5%, depending on the mass of sample.

For the current study, measurements of the heat capacity were performed in two temperature ranges in order to reach the lowest temperature possible. For each composition, two samples were selected with different masses. For the very low temperature region a smaller sample, when available, was used in order to obtain the lowest value on the temperature scale in view of the self heating effect of 239Pu. From about 22 K up to 300 K the quantity of used material was almost doubled. In Table 1 the masses of the samples used for this study are listed together with the temperature range that was covered for each composition.

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (K)</th>
<th>Mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th0.97Pu0.03O(_2)</td>
<td>7.34–21.99</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>21.99–291.94</td>
<td>27.4</td>
</tr>
<tr>
<td>Th0.92Pu0.08O(_2)</td>
<td>3.58–22.15</td>
<td>16.8</td>
</tr>
<tr>
<td></td>
<td>22.15–272.27</td>
<td>25.7</td>
</tr>
<tr>
<td>Th0.70Pu0.30O(_2)</td>
<td>6.55–22.22</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>22.22–291.91</td>
<td>20.3</td>
</tr>
<tr>
<td>Th0.46Pu0.54O(_2)</td>
<td>7.25–21.96</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>21.96–297.39</td>
<td>21.4</td>
</tr>
<tr>
<td>Th0.15Pu0.85O(_2)</td>
<td>8.05–22.07</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>21.99–296.61</td>
<td>27.4</td>
</tr>
<tr>
<td>PuO(_2)</td>
<td>5.81–30.28</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>30.44–270.49</td>
<td>16.6</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. PuO\(_2\)

The results for the heat capacity of 239PuO\(_2\) end-member are shown in Fig. 1(a) and are listed in Table 4. Our results agree very well with the available literature data for 242PuO\(_2\) by Flotow et al. [11] obtained by traditional adiabatic calorimetry on a sample of 22.5 g. These authors also measured the heat capacity of a 244PuO\(_2\) sample (3.64 g) between 4 and 25 K, obtaining very similar results and confirming the absence of anomalies. The radioactivity of 239Pu and also the minor isotope 240Pu that is present in our sample is much higher than that of 242Pu and as a result the self-heating of the sample and rapid build up of radiation-induced defects may affect the measurement. The adiabatic calorimetric measurements on 239PuO\(_2\) by Sandenaw [12] have clearly demonstrated that this could lead to anomalous and irreproducible results. A comparison of the heat capacity obtained in this study with the above mentioned literature data is shown in Fig. 2 as \( C_p/T \) against the squared temperature.

In our measurements the self-heating effect was limited by using very small amounts of samples (5.6 and 16.6 mg), and applying appropriate corrections based on the decay heat. The influence of radiation-induced defects was limited by annealing the sample just before the measurement at \( T = 1273 \) K in air for 10 h. Moreover, in the PPMS equipment the heat capacity of the sample was measured when cooling down from room temperature, starting with a pristine sample, gradually building up radiation defects that more easily survive with decreasing temperature. This is different from adiabatic calorimetry for which the sample is first brought to the lowest cryogenic temperature, where radiation defects immediately build up with a high survival rate, and the complete measurement is performed on more damaged sample.

The experimental heat capacity values in the very low temperature region (<12 K) have been fitted using the following equation:

\[
\frac{C_p}{N_fk_B} = \frac{12\pi^4}{5} \left( \frac{T}{\theta_0} \right)^3
\]  

(1)
Here, $T$ is the temperature, $N_A$ is the Avogadro number, $k_B$ is Boltzmann’s constant and $\Theta_D$ is the Debye temperature. This equation implies a linear relation between $C/T$ and $T^2$, and as shown in Fig. 2 this is indeed observed for our results for PuO$_2$. Moreover, $C/T$ nicely extrapolates to zero at $T=0$ K. Our data are slightly higher than the results of Flotow et al. for $^{242}$PuO$_2$ and
$^{244}\text{PuO}_2$, well within the uncertainties of the measurements. The results of Sandenaw for $^{239}\text{PuO}_2$ are much higher and suggest a non-zero entropy at $T=0$ K, probably resulting from radiation-induced disorder. From our data we obtain $\Theta_\theta=234.3$ K for $\text{PuO}_2$. By extrapolation of the linear relation to 0 K, we obtain for the entropy at 12 K, $S_0=0.087$ J K$^{-1}$ mol$^{-1}$, whereas Flotow et al. [11] obtained $S_0=0.051$ J K$^{-1}$ mol$^{-1}$ at the same temperature.

The absolute entropy at 298.15 K derived from our low-temperature heat capacity data is $S_{298.15}=65.79$ J K$^{-1}$ mol$^{-1}$.

3.2. The $\text{(Th}_{1-x}\text{Pu}_x)\text{O}_2$ solid solutions

The results for the low-temperature heat capacity of $\text{(Th}_{1-x}\text{Pu}_x)\text{O}_2$ solid solutions for $y=0.03$, 0.08, 0.30, 0.54 and 0.85 are shown in Fig. 1 and listed in Tables 5–9. The plots in Fig. 1 show that the heat capacity curves of the samples increase smoothly with increasing temperature and that no phase transitions or other thermal anomalies are present for the measured temperature range.

In this paper the low temperature heat capacity is described as the sum of the lattice and excess components as shown in the following equation:

$$C_T = C_{\text{latt}} + C_{\text{ext}}$$

In the actinide oxides, the lattice heat capacity is attributed principally to the lattice vibrations, while the excess heat capacity is mainly due to the contribution of the 5f electron excitation caused by the crystal field splitting [14–16], resulting in a Schottky-type anomaly. In the solid solutions, however, the excess heat capacity contains an additional contribution due to the interaction of
substitutional atoms on the crystal lattice:
\[ C_P = C_{\text{lat}} + C_{\text{Sch}} + C_{\text{mix}} \] (3)

In our work the lattice heat capacity is computed from the composition weighted average of the end-members (Neumann–Kopp).

The PuO\(_2\) lattice heat capacity was obtained after subtracting \( C_{\text{Sch}} \) calculated from the crystal field energy levels (0, 992, 1776, 2153 cm\(^{-1}\)) for the \( ^{5}I_{4} \) ground state of the 5f\(^4\) configuration [14]. For ThO\(_2\), which has a 5f\(^0\) configuration, no electronic contribution needs to be considered. The phonon contribution can be described by the harmonic crystal approximation and additional correction for internal anharmonicity of vibrational modes [17].

For computing the Neumann–Kopp data, the results of ThO\(_2\) previously measured with the same equipment as used in this work [18] and PuO\(_2\) measured in this study were used, respectively. Due to lack of experimental results below 7 K for the considered end-members, we had to extrapolate the heat capacity of ThO\(_2\) and PuO\(_2\) down to 0 K. The Debye model was used to describe this low-temperature region (0–12 K) and the heat capacity function of each individual oxide was obtained.

### 3.2.1. The low temperature range (0 < (T/K) < 25)

In this temperature range the Schottky contribution from the crystal field splitting of PuO\(_2\) is practically negligible, so any excess
heat capacity of the (Th,Pu)O₂ compositions is related to cation substitution and disorder on the crystal lattice affecting the phonon frequencies of the solid solution compared to the end members. The substitution of isovalent ions with different sizes on the cation sublattice, Pu⁴⁺ (100 pm) and Th⁴⁺ (108 pm) is changing the interatomic distances of the first nearest neighbour atoms by compression or expansion of the bonds. Small changes in the interatomic distances can lead to significant changes in the interatomic forces [19,20], particularly at low temperature where the bonds become stiffer, and thus to changes in the phonon density of

Fig. 5. Excess heat capacity evolution with temperature for all intermediate compositions. The solid curve shows the Schottky contribution obtained from that calculated for pure PuO₂ (see text) and scaled to the PuO₂ concentration in the solid solution.
states [17]. Generally this results in a positive excess heat capacity, as observed in this work.

The inset graphs of Fig. 1 clearly show a positive difference between the measured and calculated lattice heat capacity values, indicating a substantial excess contribution in this temperature interval.

Fig. 3 shows the measured heat capacity of the intermediate compositions as \( \frac{C_p}{T} \) against the squared temperature together with the data of the end-members, the heat capacity of PuO\(_2\) measured in this study and the heat capacity of ThO\(_2\) measured with the same instrument [18]. The experimental heat capacity values in the very low temperature region (\( T < 12 \) K) have been fitted using Eq. (1) to yield the Debye temperature \( \theta_D \), which is characteristic for the phonon dispersion in a solid. Its variation in the (Th,Pu)O\(_2\) system is represented in Fig. 4(a) as \( \Delta \theta_D \), showing that the Debye temperatures of the solid solution are systematically lower than the end members, which is thus a clear indication for the substantial impurity-phonon scattering occurring in this system at low temperature.

This is also evident from the entropy calculated at 12 K for each individual composition, based on the low-temperature data obtained in this study using the same approach as for the PuO\(_2\). Its variation, shown in Fig. 4(b), reveals a similar deviation from the linear interpolation of the end-members, with composition. The \( \theta_D \), \( \Delta \theta_D \), \( S_{12 \text{K}} \) and \( \Delta S_{12 \text{K}} \) values are given in Table 2.

3.2.2 The intermediate temperature range (25 < (\( T \)/K) < 250)

In this temperature range the excess contribution (Schottky) from breaking of the degeneracy of the \( ^4I_5 \) electronic ground state of the Pu\(^{4+}\) ion also needs to be considered in the analysis of the heat capacity. It should be realised that towards the end of this temperature range the excess heat capacity represents a small difference between two large numbers, and is thus subjected to increasing uncertainties. Moreover, the samples had to be encapsulated in a significant quantity of Stycast, for contamination reasons [13], and as a result a non-negligible contribution to the measured total signal was due to the encapsulation.

The comparison to the lattice heat capacity (i.e. without considering the Schottky anomaly in PuO\(_2\)) obtained from the Neu mann–Kopp’s molar additivity rule is shown in Fig. 1 and the calculated excess heat is shown in Fig. 5 as \( \Delta(C_p) = C_p^{\text{th}} - C_p^{\text{lat}} \). It can be seen that an excess contribution is present for all compositions, and it becomes more obvious with increasing PuO\(_2\) concentration. For the two samples with the highest concentration, Th\(_{0.46}\)Pu\(_{0.54}\)O\(_2\) and Th\(_{0.15}\)Pu\(_{0.85}\)O\(_2\), we observe a clear rise in the excess heat capacity above 100 K, at which the effect of the Schottky contribution is expected. For the Th\(_{0.70}\)Pu\(_{0.30}\)O\(_2\), Th\(_{0.92}\)Pu\(_{0.08}\)O\(_2\) and Th\(_{0.97}\)Pu\(_{0.03}\)O\(_2\) compositions, the excess heat capacity is constant above about 100 K, considering the accuracy in that temperature range.

It is also clear from Fig. 5 that the cation substitution and disorder on the crystal lattice are still prominent in this temperature range. From the results we thus conclude that the increase of the excess heat capacity up to 150 K is mainly due to the effect of cation substitution on the phonon modes and above this temperature the excess arising from the Schottky contribution of the 5f electrons of Pu\(^{4+}\) (crystal field splitting) is evident in the samples with high Pu concentration.

![Fig. 6. The relative excess heat capacity evolution with temperature for the investigated intermediate compositions.](image)

Table 3

<table>
<thead>
<tr>
<th>Solid solution</th>
<th>( C_p ) (298.15 K)</th>
<th>( A )</th>
<th>( B )</th>
<th>( C \times 10^{-4} )</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th(<em>{0.46})Pu(</em>{0.54})O(_2)</td>
<td>65.42</td>
<td>9.21239</td>
<td>0.43232</td>
<td>6.13153</td>
<td>37.40719</td>
</tr>
<tr>
<td>Th(<em>{0.30})Pu(</em>{0.70})O(_2)</td>
<td>67.37</td>
<td>8.2539</td>
<td>0.43232</td>
<td>5.72083</td>
<td>20.91311</td>
</tr>
<tr>
<td>Th(<em>{0.92})Pu(</em>{0.08})O(_2)</td>
<td>62.36</td>
<td>10.58597</td>
<td>0.43234</td>
<td>6.58941</td>
<td>48.14442</td>
</tr>
<tr>
<td>Th(<em>{0.97})Pu(</em>{0.03})O(_2)</td>
<td>60.72</td>
<td>11.14913</td>
<td>0.44351</td>
<td>6.88722</td>
<td>70.42444</td>
</tr>
<tr>
<td>Th(<em>{0.92})Pu(</em>{0.08})O(_2)</td>
<td>62.09</td>
<td>9.88905</td>
<td>0.43232</td>
<td>6.13153</td>
<td>37.40719</td>
</tr>
<tr>
<td>Th(<em>{0.70})Pu(</em>{0.30})O(_2)</td>
<td>65.42</td>
<td>11.14913</td>
<td>0.44351</td>
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<td>20.91311</td>
</tr>
</tbody>
</table>
obtained and is shown in Fig. 6. It indicates that the excess heat capacity is limited resolution due to the Stycast encapsulation and lower precision due to the reduced amount of materials. To obtain the result of limited resolution due to the Stycast encapsulation and lower precision due to the reduced amount of materials. The high temperature range \((T/K) > 250\)

The irregularities of the heat capacity values above 250 K are the result of limited resolution due to the Stycast encapsulation and lower precision due to the reduced amount of materials. To derive the smoothed values, the studied temperature range was
fitted by a polynomial equation together with the enthalpy data measurements (476 < (T/K) < 1790) of our previous work [10] using the simultaneous linear regression. We thus obtained the heat capacity value at \( T = 298.15 \, K \) corresponding to each intermediate composition. In Table 3 the \( C_p(T) \) values of all intermediate compositions are listed together with the constants for the fit equations of the low temperature heat capacity results obtained in this study [10].

Based on low- and high-temperature heat capacity functions, no excess heat capacity is revealed for the high temperature region, as concluded also before in our previous study.

4. Summary and conclusions

The low temperature heat capacity of \( \text{Th}_{0.97}\text{Pu}_{0.03}\text{O}_2 \) solid solution with \( y = 0.03, 0.08, 0.30, 0.54 \) and 0.85 has been measured from a minimum of 3.6 K up to about 300 K using a Quantum
Design PPMS system. The results indicate a non-ideal behaviour of the heat capacity due to the affected phonon frequencies of the solid solution compared to the end members caused by the mass difference and lattice strain (ionic radius difference) of Pu$^{4+}$ and Th$^{4+}$ substitution on the cation sublattice. This effect is the strongest at very low temperatures, and diminishes with increasing temperature. Also the effect of the Schottky contribution caused by breaking of the degeneracy of the 4$I$ electronic ground state of the Pu$^{4+}$ ion to the excess heat capacity could be demonstrated, and is evident above $T = 100$ K for the samples with 54 and 85 wt. % PuO$_2$.

The heat capacity of $^{239}$PuO$_2$ has also been measured in this
study and the results are indicating a very good agreement with the data published by Flothey et al. [11] for $^{242}$PuO$_2$ and $^{244}$PuO$_2$ over the entire temperature range, while the data presented by Sandenaw [12] are considerably higher for the temperature range up to 30 K. Sandenaw shows in his paper that the heat capacity obtained up to 100 K is irreproducible and the peaks observed are...
mainly caused by the radiation damage. With our results we confirm the absence of anomalies for the measured temperature range. The substantial residual entropy at $T=0$ K strongly suggests that his measurements were affected by radiation damage, especially below 20 K. We argue that the lattice disorder is not the source of the anomalies observed in that work, since they were not present in the low-temperature heat capacity of the (U,Am)O$_2$ system [21] that is strongly affected by the $^{241}$Am decay.

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References