

Low temperature heat capacity of PuPO_4

C. Thiriet *, R.J.M. Konings, F. Wastin

European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany

Abstract

PuPO_4 was prepared successfully by coprecipitation and its heat capacity measured between 5 K and 300 K by a hybrid adiabatic relaxation calorimeter. The standard entropy S^0 (298.15 K) of PuPO_4 was derived and a semi-empirical method was used to describe the total entropy as the sum of the lattice entropy S_{lat} and the excess entropy S_{exs} as verified for the iso-electronic lanthanide orthophosphates. Thus the standard entropies of some actinide (III) orthophosphates were estimated.

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1. Introduction

The lanthanide orthophosphates of monazite-type structure (LnPO_4 , with Ln from La to Gd) are considered as a potential nuclear waste form. Synthetic monazite shows very promising behaviour according to various criteria for a conditioning matrix such as an incorporation of a large amount of actinide (americium and plutonium) in solid solution [1–4]. The knowledge of heat capacity and entropy is indispensable for the determination of the fundamental thermodynamic functions such as the Gibbs energy e.g. to predict their stability and materials compatibility. The present study of PuPO_4 is within this context. This compound was prepared successfully from plutonium nitrate precursor by coprecipitation as presented in the first section of this paper. An intermediary compound PuP_2O_7 is formed, and its thermal reduction leads to the final com-

pound PuPO_4 , as demonstrated by Bamberger et al. [5]. The heat capacity of PuPO_4 has been measured between 5 K and 300 K by a hybrid adiabatic relaxation calorimeter. A semi-empirical approach is applied to determine the absolute standard entropy from these measurements in the second section. This approach describes the heat capacity and entropy as the sum of different components and was used previously for the lanthanide orthophosphate compounds and also for some Am(III) and Cm(III) compounds as reported in [6–8], respectively. The standard entropies of AmPO_4 and CmPO_4 are estimated in this paper on the basis of the variation of the entropy of their iso-electronic lanthanide compounds and the plutonium orthophosphate.

2. Experimental

PuPO_4 was synthesized by coprecipitation from a Pu-nitrate solution by adding Na_2HPO_4 in stoichiometric amounts [9]. The dark green precipitate was washed with water several times and next dried at 353 K and 403 K in air for 2 h each. The precipitate was milled in an agate mortar. Then the crushed powder was converted into PuP_2O_7 by heating in Ar/ H_2 atmosphere for 6 h at

* Corresponding author. Tel.: +49 7247 951 173; fax: +49 7247 951 99173.

E-mail addresses: catherine.thiriet@itu.fzk.de (C. Thiriet), konings@itu.fzk.de (R.J.M. Konings), wastin@itu.fzk.de (F. Wastin).

Table 1
The lattice parameters of PuPO₄

<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	β (°)	References
0.67605(3)	0.69820(3)	0.64497(3)	103.636(4)	Present study
0.673(2)	0.700(2)	0.642(2)	103.8(4)	Bjorklund [11]
0.6772(7)	0.6968(6)	0.6427(7)	103.7(1)	Bamberger et al. [5]

873 K. Finally PuPO₄ was formed by the thermal decomposition of PuP₂O₇ in Ar/H₂ atmosphere for 12 h at 1273 K [5,10]. For both these treatments a molybdenum crucible was used. XRD was carried out on PuPO₄ using a Siemens D500 diffractometer with an integration time of 38 h. A single phase was observed and, as expected, the final compound belongs to the monoclinic monazite phase (P2₁/n space group). The lattice parameters have been compared with those reported by Bjorklund [11] and Bamberger et al. [5] and are compiled in Table 1.

For the heat capacity measurements from 5 K and 300 K a PPMS instrument (Quantum Design) has been used following a hybrid adiabatic relaxation method. The instrument and the method have been described in [12,13] and a critical examination of the reliability of the measured heat capacity data by PPMS device was reported by Lashley et al. [14]. A discussion on the accuracy of the apparatus at ITU was presented in our previous paper [6]. The measurements have been made on a pellet piece of 5.83 mg PuPO₄ wrapped in 1.04 mg of Stycast, the heat capacity of which was measured separately and subtracted. The active sample conditioning and acquisition procedures have been described by Javorský et al. [13]. The uncertainty of the measurements is considered to be around 2%.

3. Results and discussion

3.1. Heat capacity and absolute entropy of PuPO₄

The heat capacity of PuPO₄ was measured between 5 K and 300 K as shown in Fig. 1. In the insert, it can be seen that an anomaly occurs below around 11.5 K.¹

The irregularities of the heat capacity curve beyond 150 K are the result of limited resolution due to the Stycast encapsulation and small sample size. To derive smoothed values, the studied temperature range has been divided in different parts in which the heat capacity data has been fitted by various functions. First the heat capacity data has been fitted to a polynomial function of order 6 between 20 and 300 K:

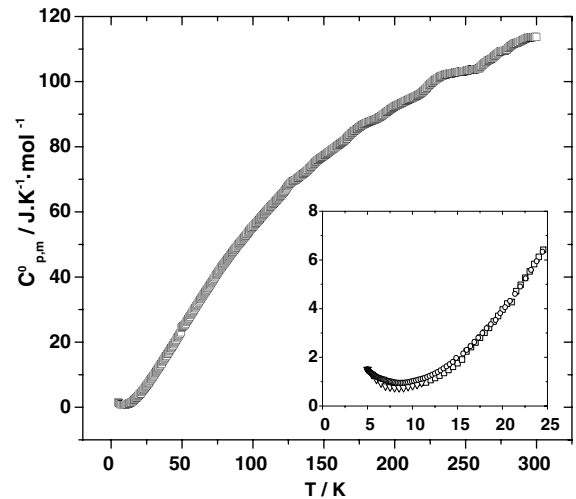


Fig. 1. The heat capacity of PuPO₄ measured by PPMS (□); in insert, zoomed curve showing the low temperature region at zero field (∇) and with an applied field of 9 T (○).

$$\begin{aligned}
 C_{p,m}^0 (\text{J K}^{-1} \text{mol}^{-1}) = & -5.77798 + 0.28489 \cdot (T/\text{K}) \\
 & + 0.01136 \cdot (T/\text{K})^2 - 1.3388 \times 10^{-4} \\
 & \cdot (T/\text{K})^3 + 6.85937 \times 10^{-7} \\
 & \cdot (T/\text{K})^4 - 1.71129 \times 10^{-9} \\
 & \cdot (T/\text{K})^5 + 1.6875 \times 10^{-12} \\
 & \cdot (T/\text{K})^6. \quad (1)
 \end{aligned}$$

From this function the heat capacity at the standard temperature $T = 298.15$ K is derived as $114.5 \text{ J K}^{-1} \text{mol}^{-1}$.

Between 11.5 K and 20 K the heat capacity has been fitted to the equation:

$$C_{p,m}^0 = \alpha \cdot T^3 + \beta \cdot T^2 \quad (2)$$

with $\alpha = 3.6 \times 10^{-4} \text{ J K}^{-4} \text{mol}^{-1}$ and $\beta = 2.73 \times 10^{-3} \text{ J K}^{-3} \text{mol}^{-1}$.

The thermal anomaly could not be characterized completely. The sample analyzed was small (5.8 mg) and measurements below 5 K are limited by the sample self-heating. However, the total entropy corresponding to the area under the curve C_p over T can be estimated theoretically as described in numerous articles [6–8,15,16]. In this approach the absolute entropy, as well as the heat

¹ The experimental data are available upon request from the authors.

capacity, are described as the sum of a lattice and an excess contribution (S_{lat} and S_{exs} , respectively). S_{lat} essentially arises from lattice vibrations, S_{exs} can have an electronic and/or magnetic origin. In the case of an electronic origin (called also a Schottky anomaly), S_{exs} is due to the presence of excited electronic levels. They arise from the ground state level splitting into several levels by the electric crystal-field (Stark effect). The excess component can also arise from a modification of the magnetic moments orientation that can be evidenced by heat capacity measurements under applied magnetic field. Therefore, we have performed measurements under different magnetic field values (0.1, 5 and 9 T) which showed that the anomaly is not affected by the field (insert in Fig. 1). Although it is difficult to definitely conclude about the origin of this thermal anomaly having only the tail of the peak, the in-field behaviour suggests that the thermal anomaly peak can not be of a magnetic ordering transition. This is different from the antiferromagnetic ordering observed in Pu_2O_3 at 17.65 K [17,18]. Therefore S_{exs} is considered here as being due to an electronic (Schottky) anomaly and defined by the Eq. (3).

$$S_{\text{exs}} = R \ln(g_0) + R \ln \left(\sum_{i=1}^n g_i e^{-\epsilon_i/RT} \right), \quad (3)$$

where ϵ_i the energy and g_i the degeneracy of level i , R is the universal gas constant and T is the absolute temperature in K.

The electronic configuration of Pu^{3+} is $6\text{H}_{5/2}$. Hence the ground state level should be split into 3 doublets due to the crystal-field effect. This assumption will be justified below.

In the lowest temperature range, the lattice contribution is practically negligible, so it can be assumed that the total entropy is due to the excess component alone and that only the ground state doublet is occupied below 11.5 K. Therefore the excess entropy is reduced to $R \cdot \ln g_0$ where g_0 is 2. Thus even though the whole thermal anomaly cannot be measured, the applied semi-empirical approach allows to deduce the total entropy value below 11.5 K i.e. $5.76 \text{ J K}^{-1} \text{ mol}^{-1}$.

On the one hand, beyond 11.5 K the total entropy can be deduced from the heat capacity functions defined in each temperature range by the Eqs. (1) and (2). Then the measured absolute entropy of PuPO_4 (S^0) corresponds to $137.0 \pm 2.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K.

On the other hand, the contribution of both components constituting S^0 (PuPO_4 , 298.15 K) can be estimated from the lanthanide compounds studies [6,7]. The lattice entropy component of PuPO_4 can be estimated by multiplying the lattice entropy component of SmPO_4 , its iso-electronic lanthanide compound, by the mean of the ratio of the lattice entropy components of various actinide compounds and their iso-electronic lanthanide compounds. The ratios for the sesquioxides,

Table 2

The heat capacity C_p in $\text{J K}^{-1} \text{ mol}^{-1}$, absolute entropy S^0 in $\text{J K}^{-1} \text{ mol}^{-1}$ and enthalpy increment $H(T) - H(20 \text{ K})$ in J mol^{-1} of PuPO_4 in function of T in K

T	C_p	S^0	$H(T) - H(20 \text{ K})$
20	3.497	6.906	0
40	16.81	13.29	200
60	30.93	22.79	678
80	44.10	33.53	1430
100	55.59	44.63	2430
120	65.33	55.66	3642
140	73.56	66.36	5033
160	80.64	76.66	6577
180	86.86	86.52	8253
200	92.41	95.97	10047
220	97.37	105.0	11946
240	101.75	113.7	13938
260	105.70	122.0	16013
280	109.7	130.0	18166
298.15	114.5	137.0	20199
300	115.1	137.7	20411

trifluorides and trichlorides are, respectively, 1.12, 1.10 and 1.09 at 298.15 K. Then we take 1.10 for the orthophosphates. From [6], the lattice entropy component of LnPO_4 is equal to $108.1 \text{ J K}^{-1} \text{ mol}^{-1}$ independent of the lanthanide element between La and Gd. Then S_{lat} (PuPO_4 , 298.15 K) is $118.9 \text{ J K}^{-1} \text{ mol}^{-1}$. If, in a first approach, the excess entropy contribution of PuPO_4 is assumed to be equal to that of SmPO_4 ($14.4 \text{ J K}^{-1} \text{ mol}^{-1}$), the calculated total standard entropy reaches $133.3 \text{ J K}^{-1} \text{ mol}^{-1}$, which is close to the experimental value (i.e. $137.0 \pm 2.7 \text{ J K}^{-1} \text{ mol}^{-1}$). The difference mainly arises from the fact that the crystal-field splitting of Pu^{3+} is likely to differ somewhat from Sm^{3+} . Table 2 collects heat capacity C_p , absolute entropy S^0 and enthalpy increment $H(T) - H(20 \text{ K})$ of PuPO_4 as function of temperature.

3.2. Standard entropy estimation of AmPO_4 and CmPO_4

The good agreement between the calculated and experimental standard entropies for PuPO_4 confirms the reliability of the followed approach. It may then be used to access the standard entropy of other actinide orthophosphates, experimentally less accessible. In this context, AmPO_4 and CmPO_4 are addressed because they have the monoclinic monazite structure [19] and they can be examined by analogy to their iso-electronic lanthanide orthophosphates studied previously [6]. The lattice entropy component for AmPO_4 and CmPO_4 is assumed to be identical to that for PuPO_4 (i.e. $118.9 \text{ J K}^{-1} \text{ mol}^{-1}$) similar to what is observed for the lanthanide orthophosphate series. In AmPO_4 , the excess entropy (S_{exs} (298.15 K)) is zero since the ${}^7\text{F}_0$ ground state of Am^{3+} is non-degenerate and the first excited

Table 3

The standard entropies and their components S_{lat} and S_{exs} of lanthanide (III) and actinides (III) orthophosphates in $\text{J K}^{-1} \text{mol}^{-1}$

	Calculated			Experimental S_{exp}	References
	S_{lat}	S_{exs}	S_{tot}		
LaPO ₄	108.1	0	108.1	108.2 ± 2.0	[6]
CePO ₄	108.1	10.5	118.6	120.0 ± 2.0	[16]
PrPO ₄	108.1	15.1	123.2		[6]
NdPO ₄	108.1	17.4	125.5		[6]
SmPO ₄	108.1	14.4	122.5		[6]
EuPO ₄	108.1	9.1	117.2		[6]
GdPO ₄	108.1	17.3	125.4	124.6 ± 2.0	[6]
PuPO ₄	118.9	14.4	133.3	137.0 ± 2.7	This study
AmPO ₄	118.9	0	118.9		This study
CmPO ₄	118.9	17.3	136.2		This study

level 7F_1 does not contribute at 298.15 K. It should be stressed that this is different for the iso-electronic Eu^{3+} cations where the 7F_1 and 7F_2 levels also contribute. In our previous paper [6] the first excited level 7F_1 has been calculated for EuPO_4 as 292, 409 and 456 cm^{-1} as well as the 7F_2 levels around 1000 cm^{-1} . However, based on the difference in energy levels values for AmCl_3 [20] (7F_1 is about 2750 cm^{-1}) and EuCl_3 [21] (7F_1 : 355.05 , 405.27 cm^{-1} and 7F_2 about 1000 cm^{-1}) our assumption is justified. Hence the standard entropy for AmPO_4 is taken to be equal to the lattice contribution only i.e. $118.9 \text{ J K}^{-1} \text{mol}^{-1}$.

The ground state of Cm^{+3} is ${}^8S_{7/2}$ and its degeneracy is 8. There is no crystal-field effect in Cm(III) as well as in Gd(III) compounds since these cations have a half filled f-shell. Their excess entropy component is only due to the independent temperature term of Eq. (3). It has been found in [6] that the whole excess contribution (i.e. $R \ln 8 = 17.3 \text{ J K}^{-1} \text{mol}^{-1}$) occurs below 12 K for GdPO_4 . Therefore S_{exs} (298.15 K) is $17.3 \text{ J K}^{-1} \text{mol}^{-1}$ for CmPO_4 also and its standard entropy is estimated to be equal to $136.2 \text{ J K}^{-1} \text{mol}^{-1}$. Table 3 compiles the standard entropies and their components (S_{lat} and S_{exs}) of the lanthanide (III) and actinide (III) orthophosphates.

4. Conclusion

PuPO_4 was synthesized successfully by coprecipitation. Its heat capacity was measured from 5 K to 300 K and indicates a thermal anomaly with a maximum below the measured temperature range. The standard entropy of PuPO_4 is derived. Using a semi-empirical method to describe the absolute entropy, it is possible to express it as a lattice and an excess values. Good agreement is found between the experimental and estimated values for PuPO_4 , showing the validity of

our estimation. From this approach, and by analogy to their iso-electronic lanthanide compounds, the standard entropies of AmPO_4 and CmPO_4 are estimated.

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