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The heat capacity of $NdAlO_3$ from 0 to 900 K

R.R. van der Laan[a,*], R.J.M. Konings[a], A.C.G. van Genderen[b], J.C. van Miltenburg[b]

[a]NRG, PO Box 25, 1755, ZG Petten, Netherlands
[b]Chemical Thermodynamics Group, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands

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Abstract

The heat capacity of neodymium aluminate $NdAlO_3$ has been measured by low-temperature adiabatic calorimetry from 4 to 420 K, yielding S^0 (298.15 K)=(99.3±0.3) J K^{-1} mol^{-1}. For temperatures up to 900 K the heat capacity has been derived from enthalpy-increment measurements (520–880 K) using high-temperature drop calorimetry. The two sets of calorimetric data are in excellent agreement and show no transition in the measured temperature range. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Neodymium aluminate; Heat capacity; Entropy; Calorimetry; Thermodynamic properties

1. Introduction

Spinel ($MgAl_2O_4$) and YAG ($Y_3Al_5O_{12}$) have been suggested as support material for uranium-free nuclear fuels for the transmutation of actinides (e.g. plutonium or americium) [1]. This support material is often called the inert matrix because it should be relatively inert with respect to neutron capture. In addition, it should also exhibit a chemically inert behaviour because the formation of new phases during irradiation may change the properties of the fuel matrix. In this respect, the possible interaction between the spinel- or YAG-matrix and the lanthanide oxides is of great relevance because the lanthanides form an important group of fission products, abundantly present in high-burnup fuels. Interaction experiments of spinel and YAG with neodymium sesquioxide (Nd_2O_3) at 1473 K, have however, shown that the neodymium aluminate ($NdAlO_3$) will be formed [2]. Knowlegde of the thermal properties of this compound is therefore important to evaluate whether this compound will be formed in an uranium-free fuel.

In a literature survey we found no experimental data for the thermal properties of $NdAlO_3$. Therefore we have measured the heat capacity of $NdAlO_3$ in the low-temperature as well as the high-temperature range, the results of which are reported in the present paper.

2. Experimental

The $NdAlO_3$ sample was prepared from Nd_2O_3 (Cerac, specified to be 99.9% pure, −325 mesh, preheated at 1073 K in pure oxygen) and Al_2O_3 (Gimex). Stoichiometric amounts of Nd_2O_3 and Al_2O_3 were mixed, pressed into pellets and heated at 1723 K in air for 50 h. After heating and grinding

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*Corresponding author. Fax: +31-224-563-608; e-mail: r.vanderlaan@nrg-nl.com

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Table 1
Experimental low-temperature heat capacity data for $NdAlO_3$

T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})
Run 1							
303.71	96.13	329.70	101.5	355.66	104.9	381.70	107.7
305.72	96.91	331.70	101.8	357.66	105.1	383.71	107.9
307.72	97.51	333.70	102.1	359.66	105.3	385.72	108.2
309.71	98.06	335.69	102.3	361.66	105.6	387.73	108.3
311.71	98.49	337.69	102.6	363.67	105.8	389.74	108.5
313.71	98.95	339.69	102.9	365.67	106.0	391.76	108.6
315.71	99.33	341.68	103.2	367.67	106.3	393.78	108.8
317.71	99.62	343.68	103.4	369.67	106.5	395.78	108.9
319.71	99.92	345.68	103.7	371.68	106.7	397.79	109.1
321.71	100.2	347.67	103.9	373.68	106.9	399.81	109.3
323.70	100.6	349.67	104.2	375.69	107.1		
325.70	100.9	351.67	104.4	377.69	107.3		
327.70	101.2	353.66	104.7	379.70	107.5		
Run 2							
283.57	94.32	317.49	99.94	352.36	104.6	387.32	108.3
285.45	94.67	319.98	100.3	354.86	104.9	389.82	108.5
287.64	95.08	322.47	100.7	357.35	105.2	392.33	108.7
290.13	95.57	324.96	101.0	359.85	105.5	394.83	108.9
292.62	96.05	327.45	101.4	362.35	105.7	397.34	109.2
295.10	96.51	329.94	101.8	364.84	106.0	399.84	109.4
297.59	96.90	332.43	102.1	367.34	106.3	402.35	109.6
300.08	97.28	334.92	102.4	369.83	106.5	404.86	109.8
302.56	97.65	337.41	102.7	372.33	106.8	407.36	110.0
305.05	97.99	339.90	103.1	374.82	107.1	409.86	110.2
307.54	98.39	342.39	103.4	377.32	107.3	412.36	110.4
310.03	98.79	344.89	103.7	379.82	107.5	414.86	110.5
312.52	99.21	347.38	104.0	382.32	107.8	417.37	110.7
315.01	99.55	349.87	104.3	384.82	108.1	419.87	110.9
Run 3							
7.14	0.07458	12.36	0.2769	17.81	0.7674	23.74	2.323
8.80	0.09636	13.69	0.3425	19.23	1.023	25.29	2.998
10.03	0.1201	15.04	0.4559	20.70	1.346	26.89	3.541
11.07	0.2213	16.41	0.5923	22.20	1.732	28.56	4.256
Run 4							
9.11	0.1366	14.89	0.4629	19.21	0.9940	23.76	2.302
11.48	0.2535	16.27	0.6031	20.72	1.347	25.34	3.026
13.38	0.3341	17.74	0.7330	22.22	1.753		
Run 5							
27.75	3.781	45.64	14.42	65.50	25.23	86.40	33.97
29.08	4.784	47.38	15.37	67.37	26.09	88.32	34.71
30.77	5.509	49.13	16.45	69.25	26.91	90.26	35.49
32.35	6.381	50.90	17.57	71.13	27.80	92.19	36.26
33.93	7.452	52.69	18.67	73.02	28.63	94.12	36.98
35.53	8.495	54.48	19.64	74.92	29.40	96.06	37.74
37.17	9.337	56.29	20.59	76.82	30.16	98.01	38.43
38.84	10.17	58.11	21.55	78.73	30.88	99.95	39.20
40.53	11.19	59.94	22.53	80.64	31.73		
42.22	12.26	61.79	23.53	82.55	32.51		
43.92	13.37	63.64	24.41	84.47	33.25		

Table 1 (*Continued*)

T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})
Run 6							
25.79	3.320	39.40	10.54	54.58	19.68	70.75	27.64
27.28	3.715	41.24	11.62	56.56	20.75	72.81	28.55
28.87	4.480	43.09	12.85	58.55	21.78	74.89	29.40
30.63	5.452	44.96	13.97	60.55	22.89	76.97	30.26
32.34	6.366	46.85	15.10	62.57	23.91	79.06	30.95
34.05	7.459	48.75	16.21	64.60	24.85		
35.80	8.626	50.68	17.46	66.64	25.77		
37.58	9.525	52.62	18.61	68.69	26.65		
Run 7							
80.73	31.96	135.59	52.87	194.62	73.27	254.10	88.35
81.09	31.93	138.04	53.76	197.09	74.02	256.59	88.80
82.49	32.50	140.48	54.67	199.56	74.74	259.08	89.32
84.91	33.42	142.93	55.59	202.03	75.49	261.57	89.85
87.29	34.33	145.37	56.53	204.50	76.21	264.06	90.39
89.66	35.23	147.82	57.39	206.98	76.94	266.55	90.89
92.04	36.19	150.27	58.33	209.45	77.58	269.04	91.47
94.43	37.10	152.73	59.27	211.93	78.33	271.53	91.98
96.82	38.03	155.18	60.12	214.41	78.94	274.02	92.54
99.22	38.91	157.64	61.02	216.88	79.62	276.51	92.98
101.62	40.14	160.10	61.89	219.36	80.29	279.00	93.49
104.03	40.90	162.56	62.77	221.84	80.96	281.50	93.97
106.43	41.85	165.02	63.62	224.32	81.56	283.99	94.45
108.84	42.74	167.48	64.45	226.80	82.23	286.48	94.91
111.26	43.66	169.94	65.29	229.28	82.89	288.98	95.44
113.68	44.55	172.41	66.10	231.76	83.54	291.47	95.89
116.10	45.46	174.87	66.97	234.25	84.13	293.96	96.31
118.53	46.38	177.34	67.85	236.73	84.73	296.46	96.79
120.96	47.30	179.81	68.64	239.21	85.31	298.96	97.21
123.39	48.19	182.27	69.42	241.69	85.94	301.46	97.54
125.83	49.17	184.74	70.21	244.17	86.48	303.96	97.94
128.26	50.15	187.21	71.00	246.65	87.08	306.46	98.29
130.70	51.07	189.68	71.74	249.14	87.64	308.97	98.68
133.15	51.97	192.15	72.54	251.62	88.18		
Run 8							
243.47	86.33	291.11	95.88	336.34	102.6	380.13	107.6
246.36	86.99	293.82	96.29	338.95	103.0	382.67	107.9
249.24	87.64	296.53	96.78	341.56	103.3	385.20	108.2
252.10	88.29	299.23	97.21	344.16	103.7	387.74	108.4
254.95	88.43	301.92	97.59	346.76	104.0	390.27	108.6
257.80	89.01	304.61	97.99	349.35	104.3	392.80	108.8
260.63	89.60	307.29	98.40	351.94	104.6	395.32	109.1
263.45	90.27	309.96	98.80	354.52	104.9	397.85	109.3
266.27	90.88	312.62	99.22	357.10	105.2	400.37	109.5
269.07	91.43	315.28	99.60	359.67	105.5	402.89	109.8
271.86	92.06	317.93	100.0	362.24	105.8	405.40	109.9
274.64	92.56	320.58	100.4	364.81	106.1	407.92	110.1
277.41	93.11	323.22	100.8	367.37	106.3	410.43	110.3
280.17	93.66	325.85	101.2	369.93	106.6	412.94	110.5
282.92	94.21	328.48	101.6	372.49	106.8	415.45	110.7
285.66	94.75	331.10	102.0	375.04	107.1	417.95	110.8
288.39	95.29	333.72	102.3	377.58	107.4	420.46	111.0

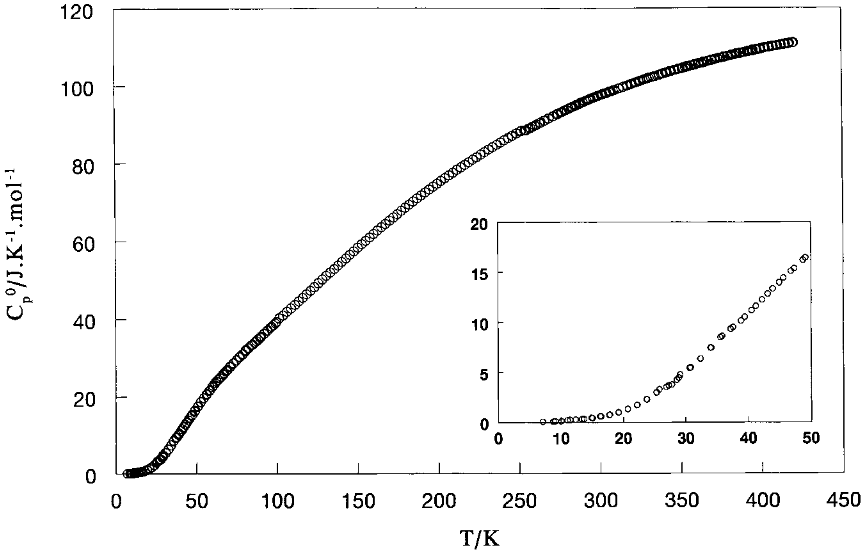

Fig. 1. Experimental heat capacity curve of $NdAlO_3$.

the phase composition of the sample was checked by X-ray diffraction analysis. This procedure was repeated three times to obtain pure $NdAlO_3$. The final X-ray pattern showed the presence of rhombohedral $NdAlO_3$ (JCPDS 39-0487) and a small amount of an impurity, very likely Nd_2O_3. Semi quantitative X-ray analysis, using small but defined additions of Nd_2O_3 to $NdAlO_3$ indicated that the amount of Nd_2O_3 in the sample is less than 0.4 mass%.

The low-temperature calorimetric measurements were performed at the Utrecht University, using the adiabatic calorimeter CAL V. Details of the equipment and its calibration have been described elsewhere [3]. The performance of the calorimeter was tested with synthetic sapphire (NIST SRM-720). The deviations between 80 and 350 K from the NIST data were well within 0.15% [3]. The weight of the sample for the low-temperature measurements was 15.9736(2) g.

The enthalpy increments were measured in an isothermal diphenyl-ether drop calorimeter, which is described in detail before [4]. The calorimeter was calibrated with synthetic sapphire (NIST SRM-720). Periodically, the performance of the calorimeter is tested, also with sapphire. The results with sapphire agree within 0.3% with the data given by NIST. For the experiment 6.6190(2) g of $NdAlO_3$ was enclosed in a quartz capsule of 1.3793(2) g.

3. Results and discussion

The low-temperature heat capacity measurements were performed in 8 runs, which are in excellent agreement with the exception of run 1. The C_p^0-values obtained in run 1 from 300 to 350 K are somewhat lower than those of run 2 and 8. As the data in run 1 from 350 to 420 K and run 2–8 are in excellent agreement, only the data for run 1 from 300 to 350 K are excluded. The data for run 1–8 are listed in Table 1 and shown in Fig. 1. The heat capacity increases smoothly from 0 to 420 K, showing no anomalies. The experimental data from 4 to 18 K have been fitted to the function $C_p^0 = \alpha T^3$, yielding

Table 2
Experimental enthalpy increments of $NdAlO_3$

T (K)	$\{H^0(T)-H^0(298.15\text{ K})\}$ (J mol^{-1})		δ (%)
	Experimental	Calculated	
524.8	24678	24645	0.13
575.8	30818	30660	0.51
626.9	36735	36805	−0.19
678.0	42869	43059	−0.44
728.8	49422	49374	0.10
779.9	55934	55821	0.20
831.2	62291	62383	−0.15
882.2	69027	68992	0.05

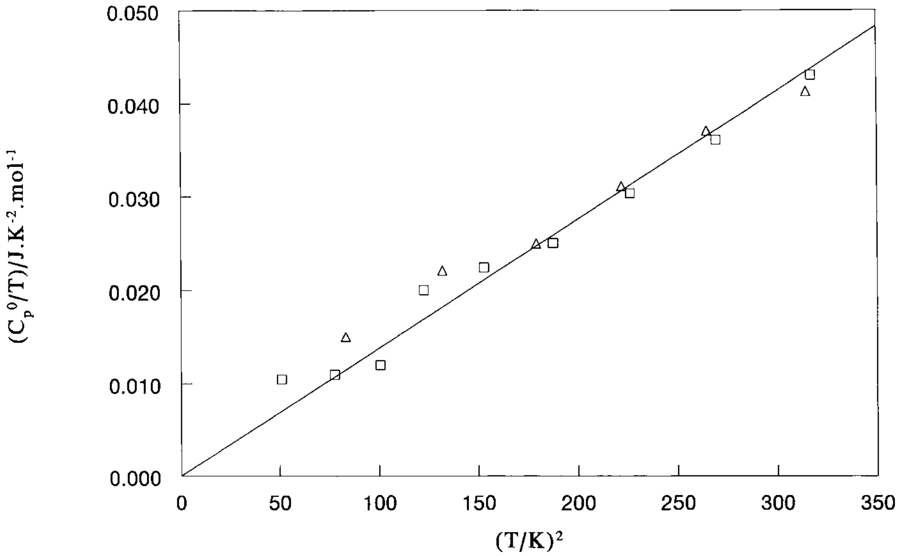

Fig. 2. Low-temperature heat capacity of $NdAlO_3$; (□) run 3; (△) run 4.

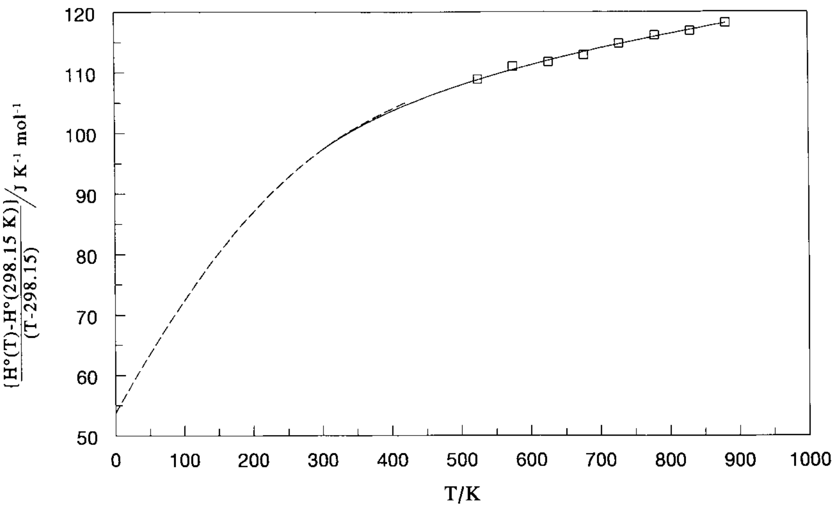

Fig. 3. The reduced enthalpy increment of $NdAlO_3$.

α=0.138×10^{-3} J K^{-4} mol^{-1} (Fig. 2). At 10 K we then obtain $C_p^0 = 0.138\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and, by integration from 0 K, S^0 (10 K)=0.046 J K^{-1} mol^{-1} and {H^0 (10 K)−H^0 (0 K)}=0.345 J mol^{-1}. These values have been used as starting values for the calculation of the thermal function from 10 to 420 K. For the values of C_p^0 and S^0 at the standard reference temperature 298.15 K, we thus obtain

$$S^0\ (298.15\,\mathrm{K}) = (99.3 \pm 0.3)\,\mathrm{J\,K^{-1}\,mol^{-1}},$$

$$C_p^0\ (298.15\,\mathrm{K}) = (97.05 \pm 0.10)\,\mathrm{J\,K^{-1}\,mol^{-1}}.$$

The results of the drop-calorimetry measurements are listed in Table 2. The data have been fitted to the

Table 3
Thermodynamic functions of $NdAlO_3$ from 0 to 900 K

T (K)	C_p^0 (J K^{-1} mol^{-1})	S^0 (298.15 K) (J K^{-1} mol^{-1})	$-\{G^0$ $(T)-H^0$ (0 K)$\}/T$ (J K^{-1} mol^{-1})	$\{H^0$ $(T)-H^0$ (0 K)$\}$ (J mol^{-1})
10	0.1380	0.0460	0.01150	0.3450
20	1.231	0.3712	0.09361	5.551
30	5.281	1.551	0.3506	36.02
40	10.93	3.823	0.9147	116.3
50	16.96	6.911	1.794	255.8
60	22.60	10.51	2.942	454.1
80	31.61	18.32	5.803	1001
100	39.35	26.19	9.094	1710
120	47.25	34.07	12.60	2577
140	54.77	41.93	16.23	3597
160	61.87	49.71	19.93	4765
180	68.50	57.38	23.67	6069
200	74.63	64.92	27.42	7501
220	80.23	72.30	31.16	9051
240	85.29	79.50	34.89	10 707
260	89.82	86.51	38.59	12 459
280	93.83	93.32	42.26	14 296
298.15	97.05	99.30	45.55	16 029
300	97.35	99.90	45.89	16 209
400	108.7	129.6	63.21	26 572
500	115.4	154.7	79.06	37 796
600	120.2	176.1	93.49	49 585
700	124.2	195.0	106.7	61 811
800	127.7	211.8	118.8	74 410
900	131.0	227.0	130.0	87 347

polynomial

$$\{H^0\ (T) - H^0\ (298.15\,\mathrm{K})\}\,\mathrm{J\,mol^{-1}} = 109.1273 \times (T\,\mathrm{K}) + 13.3640 \times 10^{-3}\ (T\,\mathrm{K})^2 + 1.78198 \times 10^6\ (T\,\mathrm{K})^{-1} - 39701.0,$$

applying C_p^0 (298.15 K) = 97.05 J K^{-1} mol^{-1} and $\{H^0$ $(T)-H$(298.15 K)$\}$=0 at 298.15 K as boundary conditions. The standard deviation of the fit is 123.6 J mol^{-1}. As shown in Fig. 3 in a plot of the reduced enthalpy increment, the high- and low-temperature ranges fit smoothly. As stated before, there are no experimental heat capacity data available to us to compare these results to. The results have not been corrected for the small amount of Nd_2O_3 in the sample, because this correction is well within the statistical error of the measurements. Only, below 25 K the correction might be somewhat larger than the statistical error, because the electronic heat capacity of Nd_2O_3 in that region is relatively high [5]. However, the effect of this on the entropy at 298.15 K is negligible.

The thermal functions of $NdAlO_3$ are listed in Table 3. For the temperature range 0–300 K these have been derived from the low-temperature measurements, for the range 300–900 K from the high-temperature measurements.

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