Calorimetric study and thermal analysis of [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O (Gly: glycin)

Bei-Ping Liu [a,b], Zhi-Cheng Tan [a,*], Xiao-Zheng Lan [a], Hua-Guang Yu [a], Da-Shun Zhang [b], Li-Xian Sun [a]

[a] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*
[b] *Department of Chemistry, Changde Normal College, Changde 415000, PR China*

Abstract

Two solid-state coordination compounds of rare earth metals with glycin, [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O were synthesized. The low-temperature heat capacities of the two coordination compounds were measured with an adiabatic calorimeter over the temperature range from 78 to 376 K. [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O melted at 342.90 K, while [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O melted at 328.79 K. The molar enthalpy and entropy of fusion for the two coordination compounds were determined to be 18.48 kJ mol^{-1} and 53.9 J K^{-1} mol^{-1} for [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$-(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O, 1.82 kJ mol^{-1} and 5.5 J K^{-1} mol^{-1} for [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O, respectively. Thermal decompositions of the two coordination compounds were studied through the thermogravimetry (TG). Possible mechanisms of the decompositions are discussed.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O; [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O; Heat capacity; Thermal decomposition; Adiabatic calorimeter; TG analysis

1. Introduction

The anticancer effect of the coordination compound of LaCl$_3$ with glycin was reported by Anghilexi [1] in 1975. From then the coordination compounds of rare earth metals with amino acid have attracted increasing interest. Many applications of these coordination compounds have been discovered [2,3]. In recent years, about 200 coordination compounds of rare earth metal with amino acid have been synthesized and studied, and structures of over 40 of these coordination compounds have been determined [4]. Few studies on thermodynamic properties, especially low-temperature thermodynamic properties of these coordination compounds have been reported in the literature.

In this paper, low-temperature heat capacities of [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and [ErY-(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O were measured with an adiabatic calorimeter over the temperature range from 78 to 376 K.

* Corresponding author. Tel.: +86-411-4379215; fax: +86-411-4691570.
E-mail address: tzc@dicp.ac.cn (Z.-C. Tan).

2. Experimental

2.1. Sample preparation and characterization

Gd(ClO$_4$)$_3$, Y(ClO$_4$)$_3$ and Er(ClO$_4$)$_3$ were prepared by reaction of corresponding oxides with aqueous solution of HClO$_4$ [5,6]. [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$]-(ClO$_4$)$_6$·5H$_2$O was synthesized by mixing mole ratio of 2:1:9 of Gd(ClO$_4$)$_3$, Y(ClO$_4$)$_3$ and glycin, and [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O was synthesized by mixing mole ratio of 1:1:6 of Er(ClO$_4$)$_3$, Y(ClO$_4$)$_3$ and glycin, respectively. The mixed solutions were stirred in water bath at 80 °C for several hours, and concentrated by evaporation at 60 °C. Afterwards, the solutions were cooled and filtered. The filtrates were kept at room temperature until crystalline products appeared. The crystals were filtered out and washed with absolute alcohol three times. Finally, the collected crystals were desiccated in a desiccator to prevent the coordination compounds from deliquescence in air.

The purities of the two coordination compounds were determined by EDTA titrimetric analysis, and the purities were 99.76 and 99.88% for [Gd$_{4/3}$-Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and [ErY(Gly)$_6$-(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O, respectively.

2.2. Adiabatic calorimeter

Heat capacity measurements were performed with a small sample automatic adiabatic calorimeter. The calorimeter consists mainly of a sample cell, an inner and outer adiabatic shields, a platinum resistance thermometer, an electric heater, two sets of differential thermocouples and a high vacuum can. The principle and structure of the calorimeter were described previously in detail elsewhere [7–9]. Liquid nitrogen was used as the cooling medium. The mass of the samples for heat capacity measurements were 2.4648 g for [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and 1.2536 g for [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O, which are equivalent to 1.668 and 0.856 mmol, based on their molar mass 1478.13 and 1465.29 g mol^{-1}, respectively. Heat capacity of the sample is derived from the total heat capacity subtracting from the total heat capacity subtracting the heat capacity of the calorimeter cell determined in a separate experiment.

To verify the reliability of the adiabatic calorimeter, the molar heat capacities for the reference standard material α-Al$_2$O$_3$ were measured. The deviations of our experimental results from the recommended values of the former National Bureau of Standards (NBS) [10] were within ±0.2% in the entire temperature range of 80–400 K.

2.3. Thermogravimetry (TG) analysis

A thermogravimetric analyzer (Model TGA/SDTA 851e, METTLER TOLEDO, Switzerland) was used for TG measurements under high purity (99.999%)
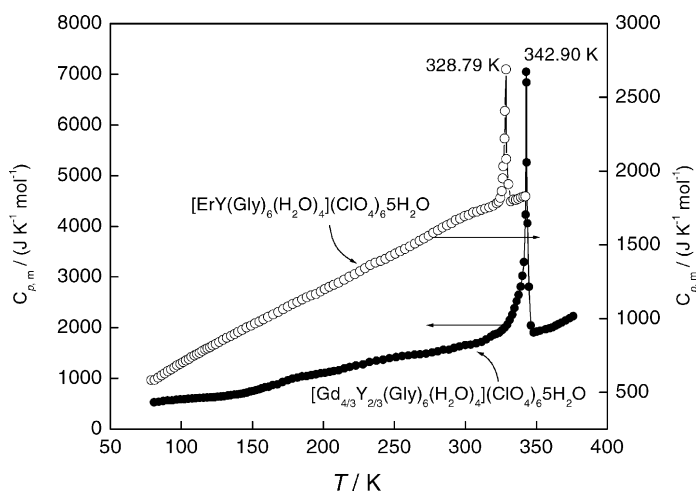

Fig. 1. Experimental molar heat capacity curves of [Gd$_{4/3}$Y$_{2/3}$(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O and [ErY(Gly)$_6$(H$_2$O)$_4$](ClO$_4$)$_6$·5H$_2$O.

nitrogen atmosphere with a flow rate of $60 \, \mathrm{ml \, min^{-1}}$. The heating rate was $10 \, °C \, \mathrm{min^{-1}}$.

3. Results and discussion

3.1. Heat capacity

The experimental molar heat capacities of the two solid-state coordination compounds of rare earth metal with amino acid are shown in Fig. 1, and tabulated in Tables 1 and 2. The molar heat capacities are fitted to the following polynomials.

For $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ over the temperature range of 80–314 and 348–376 K:

$$C_{p,m} \, (\mathrm{J \, K^{-1} \, mol^{-1}})$$
$$= 1285.7944 + 896.9624X - 381.3883X^2$$
$$- 209.6530X^3 + 482.1186X^4 + 134.0361X^5 \quad (1)$$

where $X = (T - 228)/148$, and T is the absolute temperature. The correlation coefficient of the fitted curve, $R^2 = 0.9986$.

Table 1
Experimental molar heat capacities of $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ [$M = 1478.13 \, \mathrm{g \, mol^{-1}}$]

T (K)	C_p ($\mathrm{J \, K^{-1} \, mol^{-1}}$)	T (K)	C_p ($\mathrm{J \, K^{-1} \, mol^{-1}}$)	T (K)	C_p ($\mathrm{J \, K^{-1} \, mol^{-1}}$)
80.750	530.0	174.879	961.7	314.697	1768.7
84.061	536.3	178.306	997.4	317.955	1822.6
87.294	555.4	181.701	1015.6	320.000	1860.0
90.424	562.9	185.050	1038.5	321.970	1878.8
93.481	564.6	188.356	1044.4	323.939	1899.9
96.446	580.6	191.632	1063.4	325.891	1953.8
99.356	586.7	194.865	1081.0	327.794	1999.7
102.198	591.9	198.075	1099.1	329.640	2063.8
104.980	596.8	201.240	1111.6	331.416	2154.7
107.707	601.5	204.395	1129.2	333.109	2260.4
110.381	606.7	207.512	1146.2	334.694	2386.1
113.005	610.8	211.007	1163.8	336.190	2519.0
115.592	616.6	214.868	1196.0	337.615	2649.3
118.135	620.4	218.680	1224.8	338.961	2810.5
120.642	625.9	223.014	1254.7	340.215	3024.6
123.114	630.7	227.879	1274.4	341.372	3293.9
125.550	636.9	232.672	1325.1	342.517	4230.0
127.958	644.0	237.424	1351.7	342.905	7046.4
130.335	650.1	242.045	1365.7	343.018	6839.7
132.682	658.9	246.660	1398.6	343.286	5261.2
135.005	666.5	251.212	1421.2	343.810	4059.5
137.298	677.0	255.690	1443.4	344.741	2806.1
139.572	683.2	260.076	1450.1	346.150	2043.2
141.815	694.7	264.242	1468.8	348.039	1903.3
144.039	709.4	268.258	1471.2	350.306	1921.0
146.238	721.4	272.468	1491.7	352.661	1941.0
148.414	737.2	276.590	1512.0	356.591	1967.8
150.569	753.6	280.639	1534.7	359.394	1988.9
152.703	768.5	284.608	1562.2	361.364	2007.6
154.819	783.9	288.488	1563.4	363.712	2040.4
156.917	802.8	292.252	1605.3	365.682	2070.9
158.995	826.5	295.911	1629.8	368.030	2103.7
161.531	834.6	300.000	1653.9	370.399	2140.0
164.529	867.8	303.864	1665.6	373.333	2183.3
167.813	881.7	307.727	1691.4	375.985	2227.8
171.382	930.1	311.439	1719.5		

Table 2
Experimental molar heat capacities of $[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ [$M = 1465.29\,g\,mol^{-1}$]

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
78.929	582.4	158.018	993.9	274.378	1561.4
81.266	582.8	161.257	1009.2	277.633	1580.4
83.707	599.0	164.791	1025.8	280.856	1596.8
86.082	614.1	168.280	1043.2	284.046	1616.4
88.398	627.6	171.728	1062.0	287.178	1631.8
90.659	641.5	175.134	1080.5	290.356	1645.3
92.873	653.7	178.503	1097.4	293.389	1666.3
95.038	667.4	181.832	1111.7	296.422	1676.8
97.165	680.7	185.128	1129.1	299.456	1693.3
99.252	692.1	188.393	1143.8	302.489	1700.9
101.305	703.5	191.630	1155.9	305.522	1718.9
103.323	714.0	194.838	1164.0	308.411	1723.4
105.310	725.3	198.013	1183.4	311.300	1735.4
107.267	738.6	201.158	1199.3	314.189	1745.9
109.200	748.1	204.279	1215.0	316.933	1753.4
111.104	757.7	207.370	1227.7	319.678	1763.9
112.986	766.8	210.833	1241.3	322.278	1780.5
114.844	778.3	214.656	1262.6	323.433	1792.5
116.682	788.5	218.443	1281.5	324.733	1818.0
118.499	796.6	222.189	1299.8	325.744	1863.1
120.296	805.0	225.894	1320.6	326.467	1948.7
122.073	815.9	229.544	1340.4	326.756	2031.3
124.142	825.9	233.156	1361.4	327.622	2219.0
126.714	839.6	236.767	1377.9	328.001	2407.1
129.468	855.3	240.378	1390.0	328.794	2689.1
132.187	868.0	243.844	1403.5	328.905	2081.1
134.865	880.8	247.321	1421.6	330.421	1909.7
137.509	894.8	250.798	1438.8	332.244	1794.0
140.123	907.5	254.244	1456.7	333.978	1806.0
142.972	920.9	257.670	1470.7	335.711	1803.0
146.049	937.5	261.067	1489.5	337.444	1810.5
149.093	951.0	264.439	1506.9	339.178	1819.5
152.101	966.1	267.781	1525.9	340.880	1824.8
155.076	979.2	271.096	1542.2	342.508	1826.5

For $[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, over the temperature range of 78–324, and 332–343 K:

$$C_{p,m}\ (\mathrm{J\,K^{-1}\,mol^{-1}})$$
$$= 1243.1840 + 630.6306X + 65.4433X^2$$
$$+ 86.0700X^3 - 113.0539X^4 - 91.1114X^5 \quad (2)$$

where $X = (T - 210.5)/132.5$, $R^2 = 0.9999$.

Melting was observed in the range of about 314–348 K with peak temperature 342.90 K for $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$; in the range of about 324–332 K with peak temperature 328.79 K for $[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, respectively. But we considered that the melting should be a incongruent

melting, and a dissociation reaction took place in the transition, so the liquid state was a mixture of some components different from the solid-state in structures.

3.2. Melting points, molar enthalpies and entropies of fusion

The melting temperatures of the two samples can be determined according to the C_p–T data listed in Tables 1 and 2, and corresponding C_p–T curves are shown in Fig. 1. The initial melting temperature is 314 K and the final melting temperature is 348 K, the melting peak temperature taken as
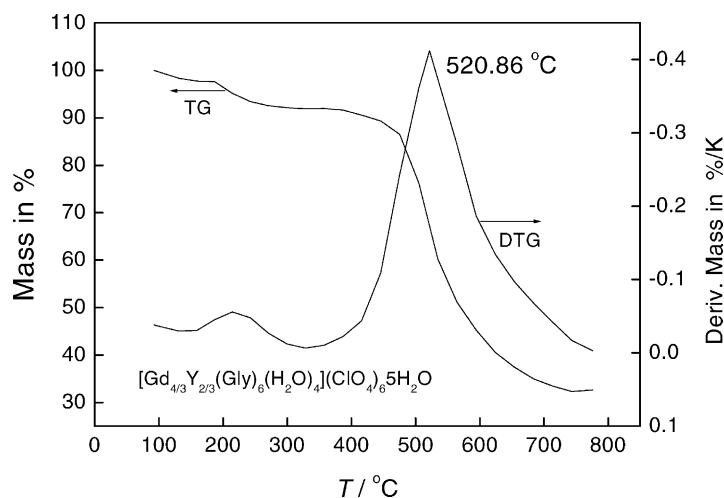
Fig. 2. TG/DTG curve of $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ under nitrogen atmosphere.

the melting point is 342.90 K for $[Gd_{4/3}Y_{2/3}$-$(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$; the initial melting temperature is 324 K and the final melting temperature is 332 K, the melting peak temperature taken as the melting point is 328.79 K for $[ErY(Gly)_6$-$(H_2O)_4](ClO_4)_6 \cdot 5H_2O$. The two samples exist in two-phase state in the temperature range of 314–348 K for $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, and of 324–332 K for $[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$.

The molar enthalpies, $\Delta_{fus}H_m$ and molar entropies, $\Delta_{fus}S_m$ of the transition can be calculated based on the following equations:

$$\Delta_{fus}H_m = \left[Q - n \int_{T_i}^{T_m} C_{p,1} \, dT - n \int_{T_m}^{T_f} C_{p,2} \, dT \right. \\ \left. - \int_{T_i}^{T_f} H_0 \, dT \right] / n \tag{3}$$
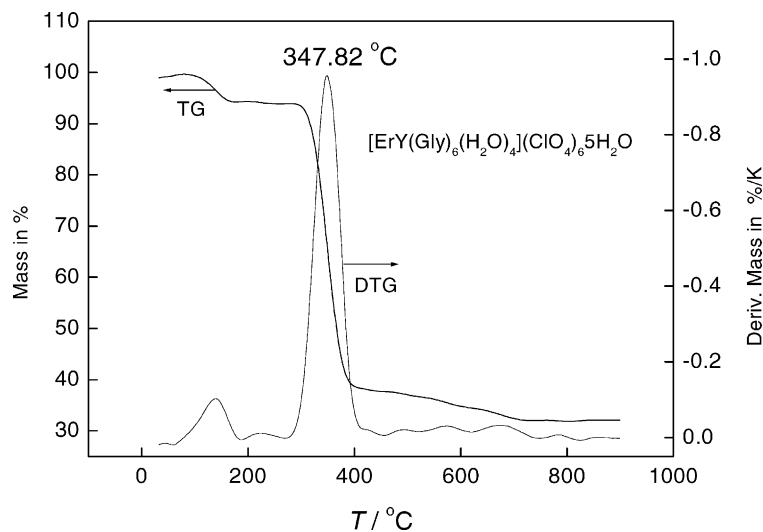
Fig. 3. TG/DTG curve of $[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ under nitrogen atmosphere.

$$\Delta_{fus} S_m = \frac{\Delta_{fus} H_m}{T_m} \qquad (4)$$

where T_i is the temperature a few degrees lower than the initial melting temperature, T_m the melting peak temperature, T_f the temperature slightly higher than the final melting temperature, Q the total energy introduced into the sample cell from T_i to T_f, H_0 the heat capacity of the sample cell from T_i to T_f, $C_{p,1}$ the heat capacity of the sample in solid phase from T_i to T_m, $C_{p,2}$ the heat capacity of the sample in liquid phase from T_m to T_f, and n the molar amount of the sample. The molar enthalpies and molar entropies of fusion for the two coordination compounds were determined to be $18.48\,kJ\,mol^{-1}$ and $53.9\,J\,K^{-1}\,mol^{-1}$ for $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$, and 1.82 $kJ\,mol^{-1}$ and $5.5\,J\,K^{-1}\,mol^{-1}$ for $[ErY(Gly)_6(H_2O)_4]$-$(ClO_4)_6 \cdot 5H_2O$, respectively.

3.3. TG analysis

The TG curve of $[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ is shown in Fig. 2. It can be seen clearly from the mass-loss curve that the most of the activities occur in the temperature range of 263–750 °C. The solid-state coordination compound was stable below 90 °C, and started decomposition at 93 °C. The total mass-loss (%) is 57.9%. We consider that the residue should be $4/3$ $GdCl_3$ and $2/3$ YCl_3 because the theoretically calculated mass-loss (%) is 56.8% if the final residues are $4/3$ $GdCl_3$ and $2/3$ YCl_3.

Fig. 3 shows that the structure of $[ErY(Gly)_6$-$(H_2O)_4](ClO_4)_6 \cdot 5H_2O$ is stable below 100 °C, it started mass-loss at 112 °C. The experiment result of final mass-loss was 61.9%, which suggested that the residual products should be $ErCl_3$ and YCl_3, because the theoretical mass-loss (%) of the decomposition is 61.9% when the final residues are $ErCl_3$ and YCl_3. According to the mass-loss in each step, the possible mechanisms of the thermal decompositions may be deduced as follows:

$[Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$

$\underset{9.5\%\,(10.96\%)}{\overset{93-320\,^\circ C}{\longrightarrow}} [Gd_{4/3}Y_{2/3}(Gly)_6(H_2O)_4](ClO_4)_6$

$\underset{57.9\%\,(56.8\%)}{\overset{386-776\,^\circ C}{\longrightarrow}} \tfrac{4}{3}GdCl_3 + \tfrac{2}{3}YCl_3$

$[ErY(Gly)_6(H_2O)_4](ClO_4)_6 \cdot 5H_2O$

$\underset{6.0\%\,(6.1\%)}{\overset{112-189\,^\circ C}{\longrightarrow}} [ErY(Gly)_6(H_2O)_4](ClO_4)_6$

$\underset{61.9\%\,(61.9\%)}{\overset{304-746\,^\circ C}{\longrightarrow}} ErCl_3 + YCl_3$
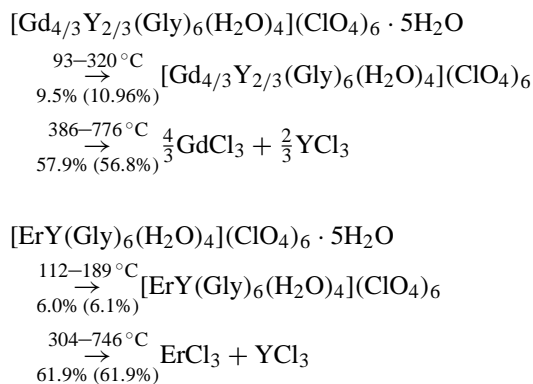
The mass-loss percentages in the brackets are the calculated theoretical values of the corresponding thermal decomposition reaction.

Acknowledgements

References

[1] L.J. Anghilexi, Arzneim Forsch 25 (1975) 793.
[2] B.S. Guo, J. Chin. Rare Earth Soc. 20 (1999) 64.
[3] T.Z. Jin, C.Q. Yang, Q.C. Yang, J.G. Wu, G.X. Xu, Chem. J. Chin. Univ. 10 (1989) 118.
[4] L.Y. Wang, F. Gao, T.Z. Jin, Chin. Chem. Bull. 10 (1996) 14.
[5] P.Y. Wei, T.Z. Jin, G.X. Xu, J. Chin. Rare Earth Soc. 10 (1992) 199.
[6] J.R. Li, X. Wang, T.Z. Jin, in: Proceedings of the Third International Conference on Rare Earth Development and Application, Baotou, China, 1995, p. 2526.
[7] Z.-C. Tan, L.X. Zhou, S.X. Chen, A.X. Yin, Y. Sun, J.C. Ye, X.K. Wang, Sci. China Ser. B 25 (1983) 1014.
[8] Z.-C. Tan, G.Y. Sun, Y. Sun, A.X. Yin, W.B. Wang, J.C. Ye, L.X. Zhou, J. Therm. Anal. 45 (1995) 59.
[9] Z.-C. Tan, G.Y. Sun, Y.J. Song, L. Wang, J.R. Han, Y.S. Liu, M. Wang, Thermochim. Acta 352–353 (2000) 247.
[10] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, J. Res. Nat. Bur. Stand. 87 (1982) 159.