Supporting Information

The "Boron Effect" on the Thermal Decomposition of Light Metal Borohydrides MBH_4 (M=Li, Na,Ca)

Flavio Pendolino

Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Cantoblanco, 28049 Madrid, Spain

flavio.pendolino@uam.es

Tables in the following pages describe temperatures which are obtained in this work (Tab. 1) and comparing with data reported in leterature (Tab. 2-4) for borohydride of litium (Li), sodium (Na) and calcium (Ca).

Table 1: Temperatures for MBH_4 and boron mixtures (M = Li, Na, Ca) under 1 bar of H_2. Melting temperature (T_m), decomposition temperature peak (T_{dp}), first decomposition peak (T_{1p}) and second decomposition peak (T_{2p}), heating rate β.

X	T_m	T_{dp}	β
		°C	°C/min
	$LiBH_4$+B		
1	285	441	1
0.8	245	289	1
0.08	240	286,430	1
	$NaBH_4$+B		
Pure	495	572	2
0.8	495	–	2
0.08	–	–	2
	$Ca(BH_4)_2$+B		
	T_{1p}	T_{2p}	β
Pure	356	384,443	2
0.8	356	432	2
0.03	357	430	2

Table 2: Phase transition (T_{Ph}), melting temperature (T_m) and decomposition temperature peak (T_{dp}) for $LiBH_4$.

	T_{Ph}	T_m	T_{dp}	β	Gas	Technique [a]
		°C		°C/min		
This work		285	441	1	H_2	Man
Pendolino[1]	111	289	491,503	11	H_2	DTA
	111	289	497,508	15	H_2	DTA
	111	289	506,517	25	H_2	DTA
Gavrichev[2]	111					DSC
Stasinevich[3]	107	282	470	5	H_2	TGA
Mitrofanova[4]	108	268	483-492	4	vac	TPD
Fedneva[5]	108	268	483-492	5	H_2	TGA
Schlesinger[6]		275		slowly		pyrolysis
Pistorius[7]	108	280		0.005		DTA

[a] Thermogravimetry analysis (TGA); Differential thermal analysis (DTA); pyrolysis, thermal decomposition in glass-tube; vacuum (vac);Manometric, pressure measurements at constant volume (Man); [b] This second decomposition step is split into two small events.

Table 3: Phase transition (T_{Ph}), melting (T_m) and decomposition temperature peak (T_{dp}) for $NaBH_4$.

	T_{Ph}	T_m	T_{dp}	β	Gas	Technique [a]
		°C		°C/min		
This work		495	572	2	H_2	Man
Johnston[8]	-83				vac	Calorimeter
Douglas [9]		497				
Stasinevich[3, 10]		505	595	5	H_2	TGA
Sterlyadkina[11]		505	565	8		TGA
Orimo[12]		496	564	10	H_2	DTA

[a]see Tab. 2

Table 4: Peak temperature of first (T_{1p}) and second (T_{2p}) decomposition for $Ca(BH_4)_2$.

	T_{1p}	T_{2p}	β	Gas	p	Technique[a]
	°C		°C/min		bar	
This work	356	384,443 [b]	2	H_2	1	Man
Kim[13]	367	397-497	5	Ar	1	DTA
Aoki[14]	367	447	5	He	1	DTA
Riktor[15]	330-380	400-480	2	vacuum	-	TPD
Rönnebro[16]	350-390	440-500	5	Ar	1	DSC

[a] see Tab. 2; [b] This second decomposition step is split into two small events.

References

[1] Pendolino, F., Mauron, P., Borgschulte, A., and Züttel, A. (2009) *J. Phys. Chem. C* **113(39)**, 17231–17234.

[2] Gavrichev, K. S. (2003) *Inorg. Mater.* **39**, S89–S112.

[3] Stasinevich, D. S. and Egorenko, G. A. (1968) *Russ. J. Inorg. Chem.* **13(3)**, 342.

[4] Mitrofanova, R., Mikhailov, Y. I., and Mal'tseva, N. (1989) *Russ. J. Inorg. Chem.* **34**, 1255 Translated from Zhuranl Neorganicheskoi Khimii 34 2207-2211 (1989) U.D.C. 621.384.8:546'34:546.271.

[5] Fedneva, E., Alpatova, V., and Mikheeva, V. (1964) *Russ. J. Inorg. Chem.* **9**, 826.

[6] Schlesinger, H. I. and Brown, H. C. (1940) *J. Am. Chem. Soc.* **62(12)**, 3429.

[7] Pistorius, C. (1974) *Z. Phys-Chem. N. Folge* **88**, 253.

[8] Johnston, H. L. and Hallett, N. C. (2002) *J. Am. Chem. Soc.* **75(6)**, 1467.

[9] Douglas, T. B. and Harman, A. W. (1958) *J. Res. Nat. Bur. Stand.* **60(2)**, 117.

[10] Johnston, H. L., Clarke, J. T., Rifkin, E. B., and Kerr, E. C. (1950) *J. Am. Chem. Soc.* **72(9)**, 3933.

[11] Sterlyadkina, Z., Kryukova, O., and Mikheeva, V. (1965) *Russ. J. Inorg. Chem.* **10**, 316.

[12] Orimo, S., Nakamori, Y., and Züttel, A. (2004) *Mat. Sci. Eng. B-solid* **108(1-2)**, 51.

[13] Kim, J.-H., Jin, S.-A., Shim, J.-H., and Cho, Y. W. (2008) *J. Alloys Compd.* **461(1-2)**, L20–L22.

[14] Aoki, M., Miwa, K., Noritake, T., Ohba, N., Matsumoto, M., Li, H. W., Nakamori, Y., Towata, S., and Orimo, S. (2008) *Appl. Phys. A* **92(3)**, 601–605.

[15] Riktor, M. D., Sorby, M. H., Chlopek, K., Fichtner, M., Buchter, F., Z uttel, A., and Hauback, B. C. (2007) *J. Mater. Chem.* **17(47)**, 4939–4942.

[16] Rönnebro, E. and Majzoub, E. H. (2007) *J. Phys. Chem. B* **111(42)**, 12045–12047.