Supporting Information
Predicting dopant activity of chemical compounds against ammonia borane with key descriptors: electronegativity and crystal structure

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I. EXPERIMENTAL METHOD

Detailed descriptions of materials used in experiments are as follows: Ammonia borane (Sigma Aldrich, 97 %), $CuCl_2$ (Sigma Aldrich, 99.995 %), Nb (Kojundo Chemical Lab., 99.99 %), NbF5 (Sigma Aldrich, 98 %), NbO (Kojundo Chemical Lab., 99.99 %), Nb2O5 (Kojundo Chemical Lab., 99.99 %), TiH2 (Sigma Aldrich, 98 %. All of the samples are handled in a glovebox filled with purified Ar atmosphere in order to prevent oxidation. Each of the above materials is mixed with ammonia borane using a planetary ball-mill apparatus (Fritsch Pulverisette 7) with 20 stainless steel balls (7 mm in diameter) and 300 mg samples (ball : powder ratio = 70 : 1, by mass). The milling process is performed under 0.1 MPa Ar atmosphere. The total milling process time and additive amount is collected in Table 1. Please note that some mixtures are prepared by hand-mixing in a glovebox where the milling time of 5 min indicates the hand mixing. Hydrogen desorption temperature of ammonia borane is analyzed by thermal mass spectrometry measurements (TDMS, ULVAC, BGM-102) combined with thermogravimetry and differential thermal analysis (TG-DTA, Bruker, 2000SA).

II. EXPERIMENTAL DATA SET

The experimental data is collected in Table 1. Sample numbers 18, 33,48,49,50,51,52,53, and 54 are experimentally performed where other samples are acquired from previous work as well as other researchers work.

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III. EXPERIMENTAL RESULT

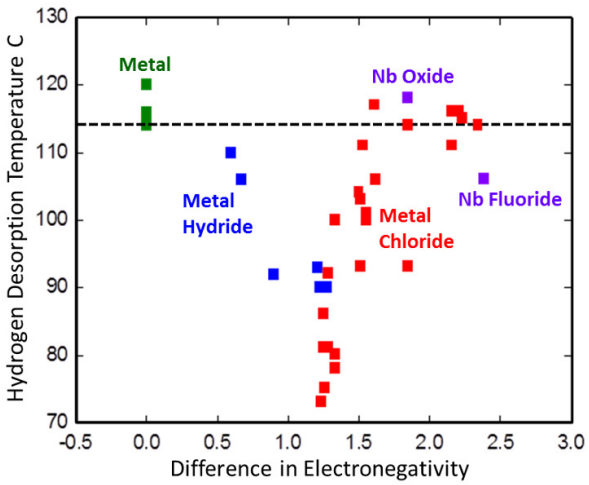

FIG. 1: The difference in electronegativity of chemical compounds and corresponding desorption temperature of ammonia borane in experiment. Data is classified by the phases of dopants. Dash line indicates the H_2 desorption temperature of ammonia borane without dopants

The difference in electronegativity of chemical compounds, which are classified by the phase of the dopant, and the corresponding desorption temperature of ammonia borane is shown in Figure 1. Please note that dispersion of metal chlorides is due to various experimental conditions of metal chlorides data sampled as seen in Table 1. However, the fundamental correlation of electronegativity and desorption temperature are the same in principle.

A. Table 1

No.	additive	Crystal Structure	milling Time	amount (mol%)	melting point	Formation enthalpy	Formation entropy	χ p of cation	χ p of anion	χ p difference	Electron affinity of cation	Electron affinity of anion	cation valence	Desorption temperature	heating rate ($^{\circ}C\ min^{-1}$)	Note
1	KCl	cubic	60	10	770	-436	83	0.82	3.16	2.34	0.5	3.61	1	114	3	Ref.5
2	NaCl	cubic	60	10	801	-411	72	0.93	3.16	2.23	0.55	3.61	1	115	3	Ref.5
3	SrCl2	monoclii	60	10	874	-829	115	0.95	3.16	2.21	0.05	3.61	2	116	3	Ref.5
4	LiCl	cubic	60	10	605	-408	59	0.98	3.16	2.18	0.62	3.61	1	116	3	Ref.5
5	CaCl2	orthorhc	60	10	772	-795	108	1	3.16	2.16	0.02	3.61	2	116	3	Ref.5
6	MgCl2	rhombol	60	10	714	-641	90	1.31	3.16	1.85	0	3.61	2	114	3	Ref.5
7	TiCl3	rhombol	60	10	425	-315	140	1.54	3.16	1.62	0.08	3.61	3	106	3	Ref.5
8	MnCl2	rhombol	60	10	654	-481	118	1.55	3.16	1.61	0	3.61	2	117	3	Ref.5
9	AlCl3	monoclii	60	10	192	-704	111	1.61	3.16	1.55	0.43	3.61	3	101	3	Ref.5
10	VCl3	hexagon	60	10	300	-581	131	1.63	3.16	1.53	0.53	3.61	3	111	3	Ref.5
11	ZnCl2	orthorhc	60	10	275	-415	110	1.65	3.16	1.51	0	3.61	2	103	3	Ref.5
12	CrCl2	orthorhc	60	10	820	-395	115	1.66	3.16	1.5	0.67	3.61	2	104	3	Ref.5
13	FeCl2	rhombol	60	10	677	-342	118	1.83	3.16	1.33	0.15	3.61	2	78	3	Ref.5
14	CoCl2	rhombol	60	10	735	-313	109	1.88	3.16	1.28	0.66	3.61	2	81	3	Ref.5
15	CuCl2	monoclii	5	1	498	-220	108	1.9	3.16	1.26	1.24	3.61	2	108	3	Ref.5
16	CuCl2	monoclii	5	5	498	-220	108	1.9	3.16	1.26	1.24	3.61	2	103	3	Ref.5
17	CuCl2	monoclii	5	10	498	-220	108	1.9	3.16	1.26	1.24	3.61	2	75	3	Ref.5
18	CuCl2	monoclii	5	20	498	-220	108	1.9	3.16	1.26	1.24	3.61	2	69	3	
19	CuCl2	monoclii	60	10	498	-220	108	1.9	3.16	1.26	1.24	3.61	2	75	3	Ref.5
20	NiCl2	rhombol	60	10	1001	-316	107	1.91	3.16	1.25	1.16	3.61	2	81	3	Ref.5
21	AgCl	cubic	60	2	1547	-127	96	1.93	3.16	1.23	1.3	3.61	1	109	3	Ref.5
22	AgCl	cubic	60	10	1547	-127	96	1.93	3.16	1.23	1.3	3.61	1	105	3	Ref.5
23	AgCl	cubic	60	20	1547	-127	96	1.93	3.16	1.23	1.3	3.61	1	73	3	Ref.5
24	FeCl2	rhombol	5	5.7	677	-342	118	1.83	3.16	1.33	0.15	3.61	2	80	1	Ref.1
25	NiCl2	rhombol	5	5.6	1001	-316	107	1.91	3.16	1.25	1.16	3.61	2	86	1	Ref.1
26	ZnCl2	orthorhc	5	5.4	275	-415	110	1.65	3.16	1.51	0	3.61	2	93	1	Ref.1
27	PtCl2	orthorhc	5	2.8	581	-123	120	2.28	3.16	0.88	2.13	3.61	2	94	1	Ref.1
28	CoCl2	rhombol	5	2.6	735	-313	109	1.88	3.16	1.28	0.66	3.61	2	92	1	Ref.2
29	FeCl3	rhombol	5	2.1	306	-399	142	1.83	3.16	1.33	0.15	3.61	3	100	1	Ref.2
30	AlCl3	monoclii	5	2.5	192	-704	111	1.61	3.16	1.55	0.43	3.61	3	100	1	Ref.2
31	MgCl2	rhombol	120	33	714	-641	90	1.31	3.16	1.85	0	3.61	2	93	5	Ref.3
32	CaCl2	orthorhc	120	33	772	-795	108	1	3.16	2.16	0.02	3.61	2	111	5	Ref.3
33	Nb	cubic	60	2	2477	0	36	1.6	-	-	0.92	-	0	120	3	
34	Ti	hexagon	60	10	1668	0	31	1.54	-	-	0.08	-	0	115	3	Ref.5
35	V	cubic	60	10	1910	0	29	1.63	-	-	0.53	-	0	116	3	Ref.5
36	Cr	cubic	60	10	1907	0	24	1.66	-	-	0.67	-	0	115	3	Ref.5
37	Mn	cubic	60	10	1246	0	32	1.55	-	-	0	-	0	116	3	Ref.5
38	Fe	cubic	60	10	1538	0	27	1.83	-	-	0.15	-	0	115	3	Ref.5
39	Co	hexagon	60	10	1495	0	30	1.88	-	-	0.66	-	0	116	3	Ref.5
40	Ni	cubic	60	10	1455	0	30	1.91	-	-	1.16	-	0	116	3	Ref.5
41	Cu	cubic	60	10	1085	0	33	1.9	-	-	1.24	-	0	116	3	Ref.5
42	Zn	hexagon	60	10	420	0	42	1.65	-	-	0	-	0	114	3	Ref.5
43	NaH	cubic	30	50	800	-56	40	0.93	2.2	1.27	0.55	0.75	1	90	2	Ref.4
44	LiH	cubic	30	50	692	-91	171	0.98	2.2	1.22	0.62	0.75	1	90	2	Ref.4
45	CaH2	orthorhc	30	50	816	-182	41	1	2.2	1.2	0.02	0.75	2	93	2	Ref.4
46	MgH2	tetragon	30	50	285	-75	31	1.31	2.2	0.89	0	0.75	2	92	2	Ref.4
47	AlH3	rhombol	30	50	150	-11	30	1.61	2.2	0.59	0.43	0.75	3	110	2	Ref.4
48	TiH2	cubic	30	50	350	-120	30	1.54	2.2	0.66	0.08	0.75	2	106	2	
49	NbF5	monoclii	60	2	73	-1814	160	1.6	3.98	2.38	0.92	3.4	5	106	3	
50	NbO	cubic	60	2	1940	-406	48	1.6	3.44	1.84	0.92	1.46	2	118	3	
51	Nb2O5	monoclii	60	1	1520	-1900	137	1.6	3.44	1.84	0.92	1.46	5	118	3	
52	AB		60	0										114	3	Ref.5
53	AB		0	0										117	3	

References

Ref.1 F. Toche, R. Chiriac, U. B. Demirci, P. Miele, International Journal of Hydrogen Energy 37, 6749 (2012).
Ref.2 R. Benzouaa, U. B. Demirci, R. Chiriac, F. Toche, P. Miele, Thermochimica Acta 509, 81 (2010).
Ref.3 Y. Li, F. Fang, Y. Song, Y. Li, Q. Zhang, L. Ouyang, M. Zhu, D. Sun, International Journal of Hydrogen Energy 37, 4274 (2012).
Ref.4 Y. Nakagawa, S. Isobe, Y. Ikarashi, S. Ohnuki, Journal of Materials Chemistry A, 2, 3926 (2014).
Ref.5 Y. Nakagawa, T. Zhang, M. Kitamura, S. Isobe, S. Hino, N. Hashimoto, S. Ohnuki, J. Chem. Eng. Data, 2016, 61 (5), 1924–129