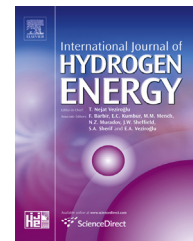


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# Thermal properties of $Y(BH_4)_3$ synthesized via two different methods

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## ABSTRACT

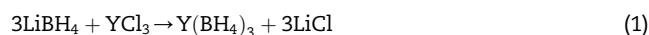
$Y(BH_4)_3$  is one of the candidates for solid-state hydrogen storage, which contains 9.06 wt% of hydrogen. In this study, the thermal properties of  $Y(BH_4)_3$  synthesized via two different methods are extensively examined. One method relies on the solid–solid metathesis reaction between  $LiBH_4$  and  $YCl_3$ , and the other method is the gas–solid reaction between  $B_2H_6$  and  $YH_3$ . The two samples are studied by differential scanning calorimetry, thermogravimetry, and X-ray diffraction. They exhibit distinctly different polymorphic phase transformation and melting. It turns out that the side product  $LiCl$  in the metathesis reaction, which has been regarded as being inert, shifts the melting point and promotes the formation of  $YB_4$  during decomposition. Differential scanning calorimetry and in situ X-ray diffraction data indicate that the addition of  $LiBH_4$  to  $Y(BH_4)_3$  induces co-melting as is found in the cases of  $LiBH_4$ – $Ca(BH_4)_2$  or  $LiBH_4$ – $Mg(BH_4)_2$ . Melt infiltration of  $Y(BH_4)_3$  into mesoporous carbon cage confirms such melting behavior.

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## 1. Introduction

For a widespread use of hydrogen as an energy carrier, an efficient and safe means of its storage is indispensable. Complex metal borohydrides,  $M(BH_4)_n$ , in general have high gravimetric and volumetric hydrogen density since cations make bondings with a complex anion  $[BH_4]^-$  having four hydrogen atoms [1,2]. Among its family,  $Y(BH_4)_3$  contains 9.06 wt% of hydrogen and its thermal stability lies between stable borohydrides such as  $LiBH_4$  or  $Ca(BH_4)_2$  and unstable ones like  $Zn(BH_4)_2$  or  $Zr(BH_4)_4$  [3–7]. Its crystal structure and

thermal properties have been identified by several experimental and theoretical studies [3,8–17]. At room temperature  $\alpha$ - $Y(BH_4)_3$  is a stable phase, but high-temperature  $\beta$ - $(BH_4)_3$  is sometimes found at room temperature due to a sluggish phase transformation [10–12]. The most common and convenient synthetic method is via the metathesis reaction between  $LiBH_4$  and  $YCl_3$  activated by ball-milling:



Accordingly, the characterization of  $Y(BH_4)_3$  mostly has been conducted under the presence of the side product  $LiCl$ .

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An attempt to obtain pure  $Y(BH_4)_3$  was made using diethyl ether as a selective solvent to exclusively dissolve  $Y(BH_4)_3$ , but the removal of LiCl was only partially achieved [9].

Recently, Remhof et al. synthesized  $Y(BH_4)_3$  via a novel method [16]. They applied the method which has been found successful in synthesizing  $LiBH_4$ ,  $Ca(BH_4)_2$ , and  $Mg(BH_4)_2$  [18,19]. The starting material is hydrided yttrium ( $YH_3$  and  $YH_2$ ), and a reactive ball-milling under  $B_2H_6/H_2$  atmosphere produces the desired compound:



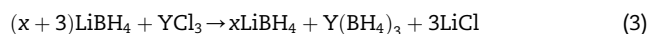
The reaction yielded about 77 wt% of  $Y(BH_4)_3$  together with unreacted  $YH_3$  and  $YH_2$  [16]. Interestingly, thermal behavior of  $Y(BH_4)_3$  from reaction (2) differs from that of  $Y(BH_4)_3$  from reaction (1). While  $Y(BH_4)_3$  from reaction (1) undergoes polymorphic phase transition from  $\alpha$ - to  $\beta$ - $Y(BH_4)_3$  at  $\sim 180^\circ C$  and its diffraction vanishes at  $\sim 200^\circ C$  [11],  $Y(BH_4)_3$  from reaction (2) remains as  $\alpha$ - $Y(BH_4)_3$  up to a higher temperature (ca.  $250^\circ C$ ) without transforming into  $\beta$ - $Y(BH_4)_3$  [16]. These observations indicate that the side product LiCl may affect the phase transition and dehydrogenation process, and that what has been known as the characteristic of  $Y(BH_4)_3$  itself might originate from the interaction with LiCl. In fact, many experimental results have highlighted the role of such side products, mostly metal halides; they can form solid solution or compound with starting materials or dehydrogenated products thereby changing thermodynamic stability and reaction path [20–26]. The starting material,  $LiBH_4$ , can also modify the thermal properties.  $LiBH_4$  may remain unreacted or can be intentionally added in excess. Jaron' et al. proposed that the acidic environment made by  $LiBH_4$  would promote decomposition of  $Y(BH_4)_3$  [14].  $LiBH_4$  may form a compound with  $Y(BH_4)_3$  as in the case of  $MSc(BH_4)_4$  ( $M = Li, Na, K$ ) [27–29] or induce low temperature melting similar to  $LiBH_4$ – $Ca(BH_4)_2$  [30,31] or  $LiBH_4$ – $Mg(BH_4)_2$  [32,33].

Toward a deeper understanding on  $Y(BH_4)_3$  and in pursuit of its further utilization, we carefully examine the thermal properties of  $Y(BH_4)_3$  synthesized via two different methods, using differential scanning calorimetry (DSC), thermogravimetry (TG), mass spectrometry (MS), and X-ray diffraction (XRD). The focus lies on the role of LiCl and  $LiBH_4$  as discussed above, which will isolate the inherent characteristics of  $Y(BH_4)_3$ .

## 2. Experimental

### 2.1. Synthesis

For the metathesis reaction, the starting materials used were commercial  $LiBH_4$  (95%, Acros) and  $YCl_3$  (99%, Sigma–Aldrich). The powders were handled in an argon-filled glove box (LABstar, MBraun,  $O_2$  level  $< 1$  ppm). Each batch was composed of about 1 g mixture of  $LiBH_4$  and  $YCl_3$ . A hardened steel vial ( $V = 100\text{ cm}^3$ ) was charged with the powder mixture and eight 12.7 mm and sixteen 7.9 mm diameter Cr-steel balls, which was then sealed with a Viton O-ring and a lid. The ball-milling was conducted using a planetary mill (Fritsch P7) at 600 rpm for 2 h. Excess  $LiBH_4$  was mixed to make a composite  $LiBH_4$ – $Y(BH_4)_3$  in varying molar ratio as follows:



where  $x$  becomes  $LiBH_4$  to  $Y(BH_4)_3$  ratio in the final product. From now on, we call this sample  $mYxLi$  ( $mY$  when  $x = 0$ ) where  $m$  stands for metathesis.

For the gas–solid reaction, elemental  $Y$  (powder, 99.9%),  $ZnCl_2$  (99.99%, Sigma–Aldrich), and  $LiBH_4$  (95%, Katchem) were the starting materials.  $YH_3$  was synthesized by hydriding yttrium under 60 bar of  $H_2$  pressure, and it was then reacted with  $B_2H_6$  generated by the decomposition of  $LiZn_2(BH_4)_5$  [34] which was made by ball-milling  $LiBH_4$  with  $ZnCl_2$ . The detailed synthesis method is described in Ref. [16]. We call this sample  $gY$  where  $g$  stands for gas. Two different batches of  $gY$  were used for this study. To make  $LiBH_4$ – $Y(BH_4)_3$  composite similar to  $mYxLi$ ,  $LiBH_4$  (95%, Acros) was added to  $gY$ . The  $Y(BH_4)_3$  content in  $gY$  (77 wt %) was taken into account when calculating molar ratio with respect to  $LiBH_4$  [16]. Small amount of  $gY$  (ca. 100 mg per batch) was milled with  $LiBH_4$  under a milder condition. A smaller hardened steel vial ( $V = 20\text{ cm}^3$ ) and five 7.9 mm diameter Cr-steel balls were used. Milling was conducted using a mixer mill (Retsch MM400) for 20 min at 30 Hz. From now on  $gYxLi$  refers to these samples where  $x$  again denotes the  $LiBH_4$  to  $Y(BH_4)_3$  ratio. In order to understand the change caused by the side product LiCl, 3 mol of LiCl (99.0%, Sigma–Aldrich) were added to the  $gY0.5Li$  sample (labeled as  $gY0.5Li3LiCl$ ).

The mesoporous CMK-3 was fabricated using SBA-15 silica as a template and sucrose as a carbon source. The SBA-15 was prepared using a triblock copolymer Pluronic P123 ( $PEO_{20}P-PO_{70}PEO_{20}$ ) as a surfactant and tetraethylorthosilicate (TEOS) as a silica source based on a previously reported procedure [35,36]. The CMK-3 was synthesized following the literature [36,37]. We repeated impregnation of aqueous sucrose solution containing sulfuric acid into the pores of calcined SBA-15 and subsequent carbonization for three times. The carbonization was completed by pyrolysis at  $700^\circ C$  in argon atmosphere. The silica template was removed by washing with hydrofluoric acid at room temperature. The final template-free CMK-3 was obtained by washing with ethanol and drying at  $120^\circ C$ .

### 2.2. Characterization

The phase composition of as-milled samples were investigated by X-ray diffraction (XRD, Bruker D8 Advance with  $Cu\ K\alpha$  radiation,  $\lambda = 1.5418\text{ \AA}$ ). All laboratory XRD measurements were performed at room temperature. A borosilicate capillary tube having a diameter of 0.7 mm and a wall thickness of  $10\text{ }\mu\text{m}$  was used as a sample holder. In situ synchrotron radiation power X-ray diffraction measurements were carried out at Pohang Accelerator Laboratory at 1D XRS KIST-PAL beamline equipped with a MAR345 CCD detector system. The selected X-ray wavelength was  $0.998398\text{ \AA}$ . The samples were mounted in a sapphire single crystal tube (o.d. =  $1.52\text{ mm}$ , i.d. =  $1.09\text{ mm}$ ), and the measurements were done under 1 bar of  $H_2$  at a heating rate of  $1^\circ C/\text{min}$ . The FIT2D program [38] was used to remove diffraction spots from the sapphire sample holder and to convert the 2D into 1D data.

Differential scanning calorimetry (DSC, Netzsch DSC 204 HP), and thermogravimetry (TG, Netzsch TG 209 F1) combined with mass spectrometry (MS, Netzsch QMS 403 C) were used to

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