



Letter

Mechanochemical synthesis of erbium borohydride: Polymorphism, thermal decomposition and hydrogen storage

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ABSTRACT

A new erbium borohydride $\text{Er}(\text{BH}_4)_3$ was synthesized from 3LiBH_4 and ErCl_3 through mechanochemical processing. This rare-earth metal borohydride presents a primitive cubic structure with $a = 10.74(1) \text{ \AA}$, which is isostructural with the one previously reported for $\text{R}(\text{BH}_4)_3$ ($\text{R} = \text{Y}$, Dy and Gd). During heating $\text{Er}(\text{BH}_4)_3$ exhibits a reversible structural transformation at about 220°C , analogous to that observed for $\text{Y}(\text{BH}_4)_3$. Combination of thermal hydrogen desorption, DSC, XRPD and FTIR measurements allows to determine that thermal decomposition of $\text{Er}(\text{BH}_4)_3$ starts at 230°C and leads to 3.2 wt% of hydrogen release obtaining ErH_2 , an unknown intermediate compound and ErB_4 . It was observed that $\text{Er}(\text{BH}_4)_3$ is partially reversible under 6.0 MPa of H_2 at 400°C and absorbs about 20% of the total hydrogen capacity obtained experimentally.

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1. Introduction

Metal borohydrides $\text{M}(\text{BH}_4)_n$ (where n indicates the valence of metal M) are being actively investigated as potential hydrogen storage materials [1,2]. Alkali and alkali-earth metal borohydrides such as LiBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ are of great interest due to their high gravimetric hydrogen storage capacities [3–5]. Unfortunately, decomposition temperatures are usually high and rehydriding only occurs under severe conditions due to the strong ionic interactions between the metal cation and the complex $[\text{BH}_4]^-$ anion. In the last years, a correlation between thermodynamical stabilities of metal borohydrides $\text{M}(\text{BH}_4)_n$ (for $\text{M} = \text{Li}$, Na, K, Cu, Mg, Zn, Sc, Zr, Hf and Ti) and cation electronegativity was experimentally and theoretically investigated [6]. The results revealed that the charge transfer from M^{n+} cations to $[\text{BH}_4]^-$ anions is a key feature for the stability of $\text{M}(\text{BH}_4)_n$. The hydrogen desorption temperature of $\text{M}(\text{BH}_4)_n$ decreases with increasing electronegativity of M. Therefore, the electronegativity is an indicator to estimate the stability of $\text{M}(\text{BH}_4)_n$. This suggests that development and investigation of new metalborohydrides may be a fruitful approach to obtain more favorable thermodynamic properties and the hydrogen release temperature.

In the search of new metal borohydrides with lower thermodynamic stabilities than those with ionic character, the rare-earth metals result interesting due to their electronegativities comprising values between 1.12 and 1.25. In the past, some of these complex hydrides were prepared by wet-chemistry routes, for example forming $\text{Ln}(\text{BH}_4)_3 \cdot 3\text{THF}$ complex ($\text{Ln} = \text{La}$, Nd, Gd, Er and Y) [7,8]. However, the elimination of the THF solvated molecules occurs at about the same temperature that hydrogen is evolved, leading to the irreversible decomposition of the borohydrides. In this context, the application of a solvent-free synthesis route such as the dry mechanochemical technique constitutes a powerful alternative [9]. This approach has recently been applied for the synthesis of rare-earth metal borohydrides $\text{R}(\text{BH}_4)_3$ ($\text{R} = \text{Y}$, Dy, Gd) by ball milling of anhydrous RCl_3 and LiBH_4 [10]. Their crystal structure was shown to have a primitive cubic structure (space group $P\bar{a}3$), with the $[\text{BH}_4]^-$ complex anions located on the edges of a distorted cube composed of R^{3+} . Frommen et al. synthesized a high-temperature (HT) structure of $\text{Y}(\text{BH}_4)_3$ (space group $Fm\bar{3}c$) by heating of $\alpha\text{-Y}(\text{BH}_4)_3$ (low temperature, LT) structure to 203°C under 10 MPa of hydrogen for 60 h and then cooling to ambient conditions [11]. In addition, HT- $\text{Y}(\text{BH}_4)_3$ was also observed at room temperature after milling of the $\text{LiBH}_4\text{-YCl}_3$ mixture [12,13] as well as after heating of LT- $\text{Y}(\text{BH}_4)_3$ to $194\text{--}216^\circ\text{C}$ [14], simultaneously with the LT- $\text{Y}(\text{BH}_4)_3$. Several studies showed that $\text{Y}(\text{BH}_4)_3$ desorbs hydrogen at temperatures $\sim 200\text{--}220^\circ\text{C}$, evidencing a lower thermodynamic stability respect to both alkali and alkali-earth metalborohydrides [11–16]. Similar thermodynamic stability was displayed by $\text{Gd}(\text{BH}_4)_3$, with decomposition starting at $\sim 210^\circ\text{C}$

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[17]. Recently, the formation of new cubic structure of $\text{Ce}(\text{BH}_4)_3$ was reported, which starts to release hydrogen at about 200 °C [18]. Following this work, the formation/decomposition of $\text{La}(\text{BH}_4)_3$ with the same structure of $\text{Ce}(\text{BH}_4)_3$, was investigated [19]. In a further study was clarified that the mechanochemical reaction between LiBH_4 and CeCl_3 leads to the formation of $\text{LiCe}(\text{BH}_4)_3\text{Cl}$ compound, the first mixed-metal and anion-substituted rare earth borohydride. $\text{LiCe}(\text{BH}_4)_3\text{Cl}$ crystallizes in the cubic space group $I43m$ [20]. No additional information was reported in the literature regarding other rare-earth metal borohydrides.

In the present paper, the new solvent-free $\text{Er}(\text{BH}_4)_3$ borohydride is synthesized by mechanochemical processing. Its crystal structure, thermal decomposition reaction and hydrogen storage properties are reported. Combination of XRD, thermal hydrogen desorption, DSC and FTIR was employed to understand the decomposition pathway and to identify the occurrence of a structural transition in $\text{Er}(\text{BH}_4)_3$.

2. Experimental

The starting materials LiBH_4 (purity $\geq 90\%$), NaBH_4 (purity $\geq 99.9\%$) and anhydrous ErCl_3 (purity: 99.99%) were purchased from Sigma-Aldrich. The $3\text{LiBH}_4\text{--ErCl}_3$ and $3\text{NaBH}_4\text{--ErCl}_3$ mixtures were mechanochemically milled at 200 rpm in argon atmosphere during 5 h using a Frisch P6 planetary mill. To avoid temperature rising during the experiment, milling times of 10 min were alternated with 10 min of rest. All materials were handled in an argon-filled glove box (MBraun Unilab) with moisture and oxygen levels below 1 ppm.

Dehydriding experiments were conducted under non-isothermal conditions (heating rates of 5 °C/min or 10 °C/min) from 20 to 400 °C using a modified Sieverts-type device coupled with a mass flow controller. The hydrogen pressure during desorption was fixed at a constant value of 0.02 MPa or 0.5 MPa. Hydrogen absorption was performed at 400 °C and 6.0 MPa of hydrogen pressure. The thermal behavior of the samples was analyzed by DSC using a heating ramp of 5 °C/min^{−1} and argon flow rate of 122 ml/min. About 5–7 mg of sample was loaded into aluminum capsules hermetically closed in the glove box. Structural changes were studied by X-ray Powder Diffraction (XRPD, Philips PW 1710/01 Instruments), using $\text{CuK}\alpha$ radiation and graphite monochromator. Cell parameter of the as-milled product was calculated with CELREF software [21]. The samples were sealed in a special holder inside the glovebox to completely prevent the reaction with air during XRPD measurements. IR spectra were obtained using FTIR Perkin Elmer Spectrum 400 spectrometer in the range of 800–4000 cm^{−1}. The gas phase released during milling and non-isothermal heating of the $3\text{LiBH}_4\text{--ErCl}_3$ mixture was collected in a degassed quartz optical cell with NaCl windows and gas phase spectra at room temperature were taken. For solid-state IR spectroscopy measurements, the selected samples were grounded with dry KBr under purified argon atmosphere, pressed to pellets and put in a specially designed cell. Handling was done inside the glove box to avoid contact with air.

3. Results and discussion

Fig. 1A shows the XRPD profiles of the $3\text{LiBH}_4\text{--ErCl}_3$ mixture after 5 h of milling. In this Figure, a new set of unidentified Bragg peaks and those corresponding to LiCl are observed. The new set of diffraction lines were assigned to a single phase compound $\text{Er}(\text{BH}_4)_3$. The structure belongs to the primitive cubic cell with a lattice constant of $a = 10.74(1)$ Å, which is isostructural to the previously reported by Sato et al. [10] for other trivalent rare-earth metal borohydrides $\text{R}(\text{BH}_4)_3$, with $\text{R} = \text{Y}$, Dy and Gd. Cell parameter of $\text{Er}(\text{BH}_4)_3$ exhibits a decrease in comparison with $\text{Gd}(\text{BH}_4)_3$ and $\text{Dy}(\text{BH}_4)_3$, in correlation with a reduction of ionic radii. No traces of the starting materials are detected. These results clearly indicate that after ball milling of $3\text{LiBH}_4\text{--ErCl}_3$ mixture for 5 h, LiBH_4 had completely reacted with ErCl_3 yielding a mixture composed by $\text{LT-Er}(\text{BH}_4)_3$ and LiCl. The metathesis reaction activated by mechanochemical processing can be described as:



Minor traces of B_2H_6 were detected by FTIR analysis in the gaseous atmosphere of the milling chamber. Additional milling for 7 h induces the apparition of some new diffraction peaks (see Supplementary material, Fig. S1). These peaks were indexed

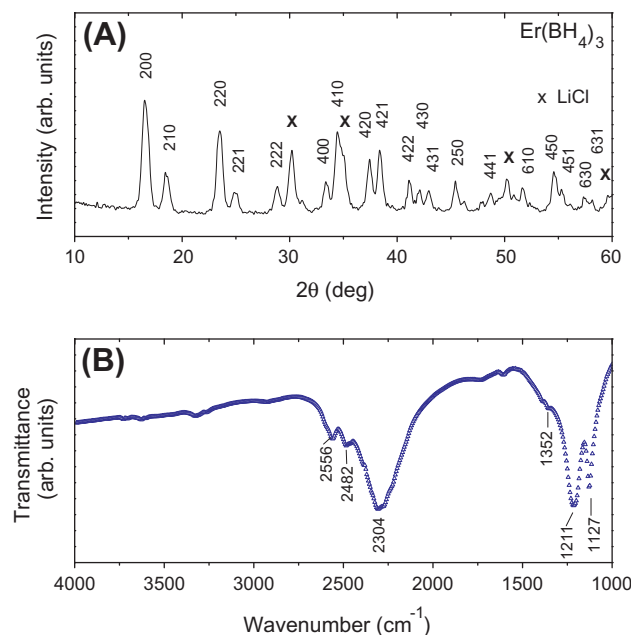
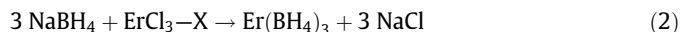


Fig. 1. (A) X-ray powder diffraction pattern of as-synthesized $\text{LT-Er}(\text{BH}_4)_3$ by mechanochemical processing of the $3\text{LiBH}_4\text{--ErCl}_3$ mixture. (B) The FTIR spectra of the $\text{LT-Er}(\text{BH}_4)_3$.

in the same cubic structure than $\beta\text{-Y}(\text{BH}_4)_3$, i.e. the high-temperature polymorph of $\text{Y}(\text{BH}_4)_3$. Therefore, in a similar way to previous investigations on $\text{Y}(\text{BH}_4)_3$ [12,13], the formation of high-temperature $\text{HT-Er}(\text{BH}_4)_3$ structure was possible via mechanochemical processing.

When NaBH_4 is used as starting material instead of LiBH_4 , the mechanochemical synthesis was unsuccessful to produce $\text{Er}(\text{BH}_4)_3$:



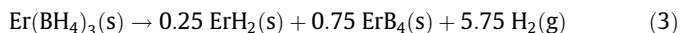
The XRPD pattern of the post-milled sample (Supplementary material, Fig. S2) evidences the strong amorphization of the sample, while the most intense diffraction peaks of NaBH_4 and YCl_3 are hardly identified. The reaction yield was unnoticeable for this sample after 5 h of milling, while no evidence of the NaCl formation was detected.

Synthesis of $\text{Er}(\text{BH}_4)_3$ was also confirmed by infrared spectroscopy. The vibrational spectra of $\text{LT-Er}(\text{BH}_4)_3$ is shown in Fig. 1B. The B–H stretching modes are split into three groups at about 2556, 2482 and 2304 cm^{−1} (Fig. 1B). In addition, strong B–H bending bands at 1127 and 1211 cm^{−1} are identified as well as an incipient band around 1352 cm^{−1}. The position of these bands yields excellent resemblance with the previously reported for $\text{LT-Y}(\text{BH}_4)_3$ produced by ball milling [16].

Thermal decomposition of the $\text{LT-Er}(\text{BH}_4)_3$ was investigated by combination of non-isothermal hydrogen desorption and DSC measurements. Fig. 2 shows the amount of hydrogen desorbed under 0.02 MPa of hydrogen pressure. The hydrogen desorption started at 230 °C; this temperature was similar than the initial dehydriding temperature for analogous rare-earth metal borohydride [11–20]. The total amount of hydrogen released after heating up to 400 °C was 3.2 wt%, taking into account the total mass of the $\text{Er}(\text{BH}_4)_3\text{--LiCl}$ mixture. This amount corresponds to 5.1 wt% when the estimation is made respect to $\text{LT-Er}(\text{BH}_4)_3$. Diborane (B_2H_6) and other gas impurities were not detected by gas FTIR during thermal treatment up to 400 °C, thus only hydrogen release take place during heating process. This is one of the conditions for reversible hydrogen storage in borohydrides. Moreover, multiple peaks observed in DSC curve evidence the complexity of the

thermal decomposition process of $\text{LT-Er(BH}_4)_3$, similar to those occurring for other complex borohydrides [11–20].

Extra XRPD measurements were done to obtain information on the dehydrogenating steps. The $\text{LT-Er(BH}_4)_3$ was heated to different temperatures in correlation with DSC curve and subsequently cooling down to room temperature. The XRPD profiles of the samples at each temperature are shown in Fig. 3. In all XRPD patterns the presence of LiCl is clearly identified. As compared to the diffraction peaks of the as-milled $\text{LT-Er(BH}_4)_3$ (Fig. 3a), some additional diffraction peaks appear in the sample heated at 220°C (Fig. 3b). Taking into account the absence of hydrogen desorption up to 230°C , the presence of an endothermic peak before this temperature (Fig. 2) and the previous structural transformation observed during milling, these peaks can be indexed based on the same cubic cell as reported for $\beta\text{-Y(BH}_4)_3$ [11]. Then, the endothermic peak between 210 and 230°C could be at least partially associated with the LT to the HT structural transition of $\text{Er(BH}_4)_3$. After non-isothermal heating up to 250°C , a 0.6 wt\% of hydrogen release occurs and a second endothermic peak is identified. In correlation, the diffraction peaks of $\text{Er(BH}_4)_3$ disappeared while those of the ErH_2 together with some unidentified peaks are detected (Fig. 3c). These unidentified peaks could imply the formation of an intermediate phase. It seems likely that Er-B-H containing species are formed during the decomposition of $\text{Er(BH}_4)_3$, by analogy to those found in other borohydrides [19,20]. When the temperature is increased up to 400°C , the complete decomposition of $\text{Er(BH}_4)_3$ occurs. The diffraction peaks observed in Fig. 3d are weak and the background suggests the presence of an amorphous phase. From Fig. 3e, this background could partially be associated with the formation of ErB_4 , which is visibly detected as a crystalline phase at 500°C . In opposition, in these last two XRD patterns (Fig. 3d and e) the peaks corresponding to ErH_2 are not clearly observed, while the most intense diffraction peak of ErH_2 (i.e. $2\theta = 30.19^\circ$) is superimposed with that of LiCl . In fact, the progress of the $\text{Er(BH}_4)_3$ decomposition between 250°C and 400°C could involve the complete disappearance of the Er-B-H intermediate compound as well as the partial consumption of the ErH_2 . Then, as temperature increases the amount of ErH_2 decreases, probably influencing the crystallinity of ErH_2 . Taking into account that from XRPD the formation of ErH_2 and ErB_4 is identified (Fig. 2d) and total hydrogen released at 400°C is 3.2 wt\% (Fig. 1A), the following reaction could be proposed as overall dehydrogenation path for $\text{Er(BH}_4)_3$:



Theoretical amount of hydrogen released from $\text{Er(BH}_4)_3$ according to reaction (3) is about 3.4 wt\% , when the presence of LiCl is considered (5.4 wt\% respect to $\text{Er(BH}_4)_3$). The actually measured value of 3.2 wt\% is in good agreement with that calculated for reaction (3).

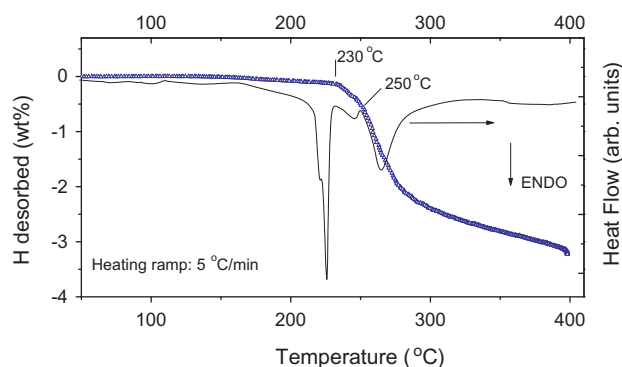


Fig. 2. Non-isothermal hydrogen desorption and DSC curve of as-synthesized $\text{LT-Er(BH}_4)_3$.

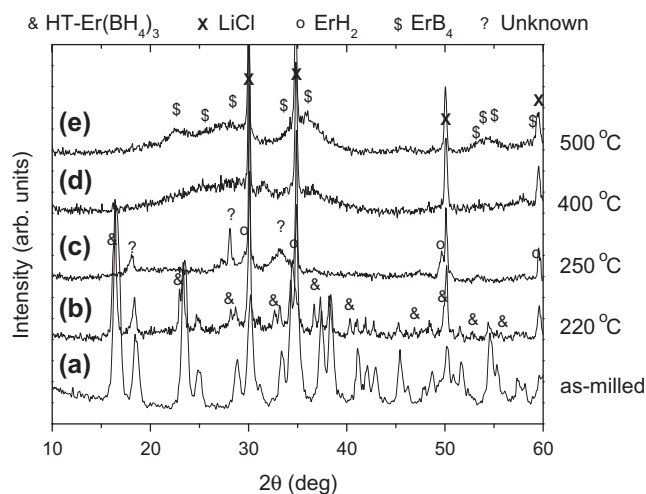


Fig. 3. X-ray powder diffraction patterns of: (a) as-synthesized $\text{LT-Er(BH}_4)_3$ and heated up to, (b) 220°C , (c) 250°C , (d) 400°C and (e) 500°C .

Additional DSC measurements were performed to corroborate the nature of the first endothermic event observed at about 220°C (Fig. 2). The as-milled $\text{LT-Er(BH}_4)_3$ was submitted to two consecutive thermal cycling (Fig. 4): first, a heating up to 225°C and cooling down to 80°C ; second, a heating up to 400°C . For comparison, the reference DSC curve for the as-synthesized $\text{LT-Er(BH}_4)_3$ is included (Fig. 4a). It is clearly observed from Fig. 4b that the first endothermic peak at 220°C is reversibly during cooling. In fact, the second cycle clearly displays practically the same thermal decomposition curve than that of the as-milled sample (Fig. 4a). This experimental behavior, in combination with XRPD data (Fig. 3b), demonstrate that the first endothermic peak involves the structural transition from the low to high temperature modification of $\text{Er(BH}_4)_3$. However, due to the shape of the first peak where two events seems to be superimposed (see Fig. 4a), the simultaneous occurrence of the $\text{Er(BH}_4)_3$ melting cannot be ruled out. On the other hand, Fig. 4c shows the thermal behavior of the sample heated at 250°C and cooled down at room temperature (XRPD shown in Fig. 3c). The thermal behavior corresponds to the third endothermic peak, verifying that this sample constitutes an intermediate phase containing hydrogen. Therefore, XRPD and

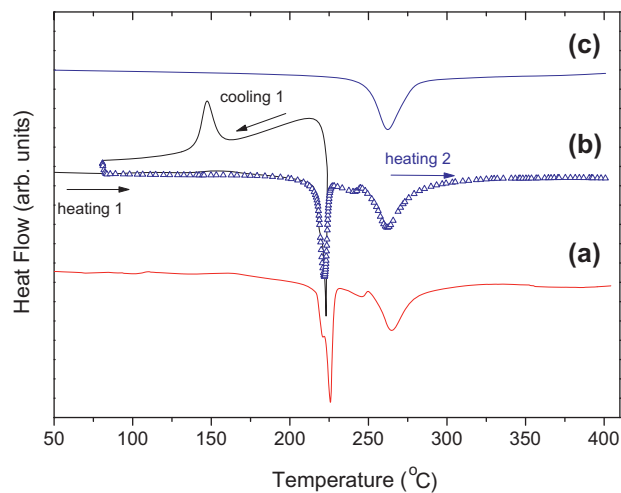


Fig. 4. DSC curves of: (a) as-synthesized $\text{LT-Er(BH}_4)_3$; (b) as-synthesized $\text{LT-Er(BH}_4)_3$ heated to 225°C , cooled down to 80°C and heated again to 400°C ; (c) $\text{LT-Er(BH}_4)_3$ pre-heated at 250°C .

DSC studies (Figs. 3 and 4) evidence the multi-step nature of the dehydriding process of $\text{Er}(\text{BH}_4)_3$.

Hydrogen storage reversibility of $\text{Er}(\text{BH}_4)_3\text{--}3\text{LiCl}$ was explored using a Sieverts-type apparatus. The sample was first heated up to 400 °C at a heating rate of 10 °C/min under 0.5 MPa of hydrogen pressure, and 3.4 wt% of hydrogen was released (about 5.4 wt% of hydrogen respect $\text{Er}(\text{BH}_4)_3$). After rehydriding at 400 °C and 6 MPa of hydrogen pressure during 6 h, a second dehydriding run was performed up to 400 °C under 0.5 MPa. The hydrogen desorbed after the second run was 0.7 wt% (see Supplementary material, Fig. S3), which corresponds to ~20% of the initial hydrogen release obtained after the first dehydriding run and demonstrates that the system is only partially reversible. Similar behavior was previously observed for analogous trivalent rare-earth metal borohydrides [13,15,17]. To transform the $3\text{LiBH}_4\text{--ErCl}_3$ mixture in a more attractive material for hydrogen storage and by analogy with $\text{LiBH}_4\text{--RCl}_3$ systems ($\text{R} = \text{Ce, Gd, La, Y}$) [13,22,23], the stoichiometry of the initial mixture could be changed to influence the nature of the decomposition products and to improve the reversibility.

4. Conclusions

$\text{Er}(\text{BH}_4)_3$ is a new example of rare-earth metal borohydride synthesized by mechanochemical process of the $3\text{LiBH}_4\text{--ErCl}_3$ mixture. The material crystallizes in the cubic space group $Pa\bar{3}$ with $a = 10.74(1)$ Å, which is isostructural with the one previously reported for $\text{R}(\text{BH}_4)_3$ ($\text{R} = \text{Y, Dy and Gd}$). Moreover, the preparation of $\text{Er}(\text{BH}_4)_3$ from the $3\text{NaBH}_4\text{--ErCl}_3$ mixture by dry-milling was unsuccessful.

Decomposition and rehydriding behavior of $\text{Er}(\text{BH}_4)_3$ was studied by using a combination of XRPD, thermal analysis, infrared spectroscopy and volumetric measurements. The material was found to exist in a low-temperature distorted modification that exhibits a phase transition to an ordered high-temperature phase, isostructural to that reported for $\text{Y}(\text{BH}_4)_3$. This structural transition is favored by heating up to 220 °C or by prolonged milling. Dehydriding of $\text{Er}(\text{BH}_4)_3$ started at 230 °C and leads to 3.2 wt% of hydrogen release obtaining ErH_2 , an unknown intermediate compound Er--B--H and ErB_4 . No diborane or other impurities gases were detected during heating. $\text{Er}(\text{BH}_4)_3$ shows partial reversibility and reabsorbs about 20% of its original hydrogen content at 400 °C and 6.0 MPa of hydrogen. The current study provides information on the structure, thermal stability and the hydrogen storage reversibility of a new rare-earth metal borohydride, enriching the literature available on related materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jallcom.2013.07.012>.

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