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In situ investigations of bimetallic potassium erbium borohydride

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ABSTRACT

Research on rare earth (RE) borohydrides is increasing due to their potential as possible hydrogen storage materials and as solid-state Li-ion conductors for battery applications. In this work, we report the formation of a new bimetallic RE borohydride, $\text{KEr}(\text{BH}_4)_4$, via mechanochemical reaction between KBH_4 and $\text{Er}(\text{BH}_4)_3$ in a molar ratio of 1:1. Post-annealing of the ball-milled mixture at 175 °C for 12 h under 40 bar of hydrogen resulted in an almost phase pure material. $\text{KEr}(\text{BH}_4)_4$ is isostructural to $\text{NaSc}(\text{BH}_4)_4$ with lattice parameters of $a = 8.4472(8)$ Å, $b = 12.4292(11)$ Å, $c = 9.6252(9)$ Å and space group Cmcm . An amorphization of the new bimetallic phase was observed at -170 °C under 1 bar argon via temperature programmed photographic analysis, which is in agreement with *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD) as well as thermogravimetric and differential scanning calorimetry (TG-DSC). The *in situ* SR-PXD data did not show decomposition into the starting monometallic borohydrides.

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Introduction

Metal hydrides are used in technological applications, where the largest commercial success has been the nickel-metal hydride battery (Ni-MH), with over 1 billion cells sold in 2015 [1]. In Ni-MH batteries, rare earth based metal hydrides related to LaNi_5H_x , are employed for the anode [2,3]. Complex metal hydrides based on rare earth metals and boron also show great potential [4,5], for example rare earth (RE) borohydrides have received an increasing amount of interest as solid state hydrogen storage materials [6–26], solid state electrolytes [27–31], luminescent [32] and magnetocaloric materials [33,34] during the past 10 years, and many new compounds and crystal structures of RE based hydrides have been extensively studied [35].

RE borohydrides show a big variety of crystal structures and can be categorized as follows. The early lanthanides La, Ce, Pr and Nd form $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ complexes in space group $I-43m$ [11,19]. The $\text{RE}(\text{BH}_4)_3$ with RE = La, Ce crystallize in $R-3c$ [36], respectively. Pr, Nd, Sm, Gd, Tb, Er, and Yb form $\alpha\text{-RE}(\text{BH}_4)_3$ ($Pa-3$) with a polymorphic phase transition to $\beta\text{-RE}(\text{BH}_4)_3$ for Y, Er, Yb ($Pm-3m/Fm-3m$) [8,10,12,19,23]. The smallest lanthanides Yb and Lu form $[\text{RE}(\text{BH}_4)_4]^-$ complex anions which are stabilized by Li^+ cations (space group $P-42c$), and they are in analogy to $\text{MSc}(\text{BH}_4)_4$ ($M = \text{Li, Na, K}$) [7,21,37,38]. Trivalent borohydrides with Sm and Eu are reduced to $\text{RE}(\text{BH}_4)_2$ upon heating, which are isostructural to $\text{Sr}(\text{BH}_4)_2$ ($Pbcn$) [20]. Recently the bimetallic $\text{NaLa}(\text{BH}_4)_4$ and $\text{K}_3\text{La}(\text{BH}_4)_6$ with space groups $Pbcn$ and $P2_1/n$, respectively, have been reported [39].

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In this study, we report on the synthesis and thermal properties of a new bimetallic borohydride, $\text{KEr}(\text{BH}_4)_4$. This compound was obtained through a combination of mechanochemical synthesis followed by thermal treatment. Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) in combination with *in situ* SR-PXD have been used to elucidate the decomposition pathway in order to determine reaction products and intermediates.

Experimental

KBH_4 (95%), ErCl_3 (99.9%), LiBH_4 (95%) and dimethyl sulfide (DMS, anhydrous, 99.9%) were purchased from Sigma Aldrich. All sample preparation and synthesis of $\text{Er}(\text{BH}_4)_3$ were carried out according to the procedures described in Ref. [23].

$\text{Er}(\text{BH}_4)_3$ and KBH_4 were ball milled in a molar ratio of 1:1 and post annealed at 175 °C for 12 h under 40 bar of hydrogen in a Sieverts type apparatus [40]. Ball milling was carried out using a Fritsch Pulverisette 6 planetary mill with an 80 ml tungsten carbide coated steel vial and balls. A ball to powder ratio of 40:1 and milling times of 1 h (4×15 min with 5 min breaks) were employed. All sample handling was executed under inert conditions with O_2 and H_2O levels kept below 1 ppm, in an MBraun glove box.

Powder X-ray Diffraction (PXD) data were collected using a Bruker AXS D8 Advance. The data were collected in transmission mode with $\text{CuK}\alpha$ $\lambda = 1.5418 \text{ \AA}$, a Göbel mirror and a LynxEye™ 1D strip detector. The samples were contained in 0.5 mm sealed boron glass capillaries.

In situ SR-PXD data were collected at the Swiss Norwegian Beam Line (SNBL), BM01A at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Sapphire capillaries with 1.2 mm and 0.8 mm outer and inner diameter were connected to an in-house manufactured remote controlled gas rig and high pressure manifold cell. The sample-to-detector distances were 146 and 345.8 mm, respectively, and the wavelength was 0.77787 Å, calibrated from a NIST LaB_6 standard. Data were collected using a Pilatus 2M detector. The exposure time was set to 30 s giving a temperature resolution of 2.5 °C/pattern and the sapphire capillary was rotated by 10° during exposure to improve powder averaging. Single crystal reflections from the sapphire tube were masked manually in Fit2D and Bubble [41,42]. Rietveld refinements were performed using GSAS and Expgui software [43,44]. The Bragg peak profiles were modelled with a Thompson-Cox-Hastings pseudo-Voigt function with three Gaussian and one Lorentzian parameter [45]. The background was fitted with a shifted Chebyshev polynomial with up to 36 terms. Atomic positions for $\text{KEr}(\text{BH}_4)_4$ and KBH_4 were taken from Refs. [37,46,47]. The crystal structure of $\text{KEr}(\text{BH}_4)_4$ was refined with the data shown in Fig. 3 at room temperature (RT). BH_4 units were treated as rigid bodies with B–H distances of 1.13 Å.

Simultaneous thermogravimetric and differential scanning calorimetry (TG-DSC) experiments were conducted using a Netzsch STA 449 F3 Jupiter analyzer. The samples were loaded in Al pans (~5–10 mg) and heated from RT to 400 °C at a heating rate of 5 °C min^{-1} . Furthermore, the annealed sample was heated from RT to 200 °C and cooled down to 60 °C at a rate of 5 °C min^{-1} . The Ar purge gas rate was set to 50 ml min^{-1} and the protection gas flow to 20 ml min^{-1} .

Temperature programmed desorption (TPD-MS) was performed in an in-house manufactured apparatus connected to a MKS Microvision-IP Residual Gas Analyser. The powder was loaded in a steel sample holder (~10 mg) and heated from RT to 400 °C with a heating rate of 5 °C min^{-1} under dynamic vacuum.

Temperature programmed photographic analysis (TPPA) was conducted on the ball milled sample. Approximately 30 mg of the powder was pressed using a pressing die and a pellet with diameter of 6 mm was prepared. The pellet was transferred to a glass tube and sealed under argon. The glass tube was placed in a home-built aluminum heating block as described in Ref. [48] and a camera was placed in front of the sample. Sample was heated from RT to 500 °C with a heating rate of 5 °C/min, while photos of the sample were collected every 5 s.

Results and discussion

Er(*BH*₄)₃ + *KBH*₄ as milled

Fig. 1a shows *in situ* SR-PXD data of the as milled $\text{Er}(\text{BH}_4)_3 + \text{KBH}_4$ from RT to 600 °C, whereas Fig. 1b presents the SR-PXD data at selected temperatures between RT and 600 °C for a better visualization. Only Bragg peaks of two phases $\text{Er}(\text{BH}_4)_3$ and KBH_4 are present at RT. Upon heating, at 97 °C the Bragg peaks of $\text{KEr}(\text{BH}_4)_4$ (two Bragg peaks shown by black arrows in Fig. 1a) are increasing in intensity and reach their strongest intensity at 168 °C (blue curve) while peak intensities for the reactants $\text{Er}(\text{BH}_4)_3$ and KBH_4 are decreasing. The Bragg peaks for the bimetallic phase resembles those of $\text{NaSc}(\text{BH}_4)_4$ and $\text{KHo}(\text{BH}_4)_4$ [37,46], thus indicating an isostructural relationship. The Bragg reflections of $\text{KEr}(\text{BH}_4)_4$ decrease rapidly from 168 °C and disappear at 176 °C (magenta curve) with diffuse scattering appearing. Simultaneously, peak intensities for KBH_4 and $\text{Er}(\text{BH}_4)_3$ are rapidly decreasing.

Once the Bragg reflections of $\text{KEr}(\text{BH}_4)_4$ have disappeared, peak intensities for KBH_4 remain stable, whereas peak intensities for $\text{Er}(\text{BH}_4)_3$ continue to decrease and are no longer detected at 260 °C. This shows that $\text{Er}(\text{BH}_4)_3$ is decomposed. Between 300 and 600 °C the diffuse scattering decreases and Bragg peaks of ErH_2 appear (green and dark blue curve in Fig. 1). From 572 to 600 °C peak intensities for KBH_4 are decreasing, which is in agreement with the reported decomposition temperature for KBH_4 of 584 °C [49]. However, traces of KBH_4 remains visible during the timeframe of the measurement.

TPPA was performed on a pressed pellet of ball-milled mixture of $\text{Er}(\text{BH}_4)_3 + \text{KBH}_4$ to investigate whether the disappearance of Bragg peaks from $\text{KEr}(\text{BH}_4)_4$ around 170 °C was due to melting. The pellet shows a color change around 176–183 °C corresponding to the formation of $\text{KEr}(\text{BH}_4)_4$. However, no melting was observed and the sample was decomposed upon further heating to 500 °C, thus showing that the loss of crystallinity is due to a solid-state amorphization. Selected TPPA pictures are shown in the supplementary information (Fig. A2).

The combined TG-DSC data for the as milled mixture of $\text{Er}(\text{BH}_4)_3$ and KBH_4 are presented in Fig. 2a. In the DSC trace a

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