Hydrogen Storage

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Potassium-Modified $Mg(NH_2)_2/2\,LiH$ System for Hydrogen Storage**

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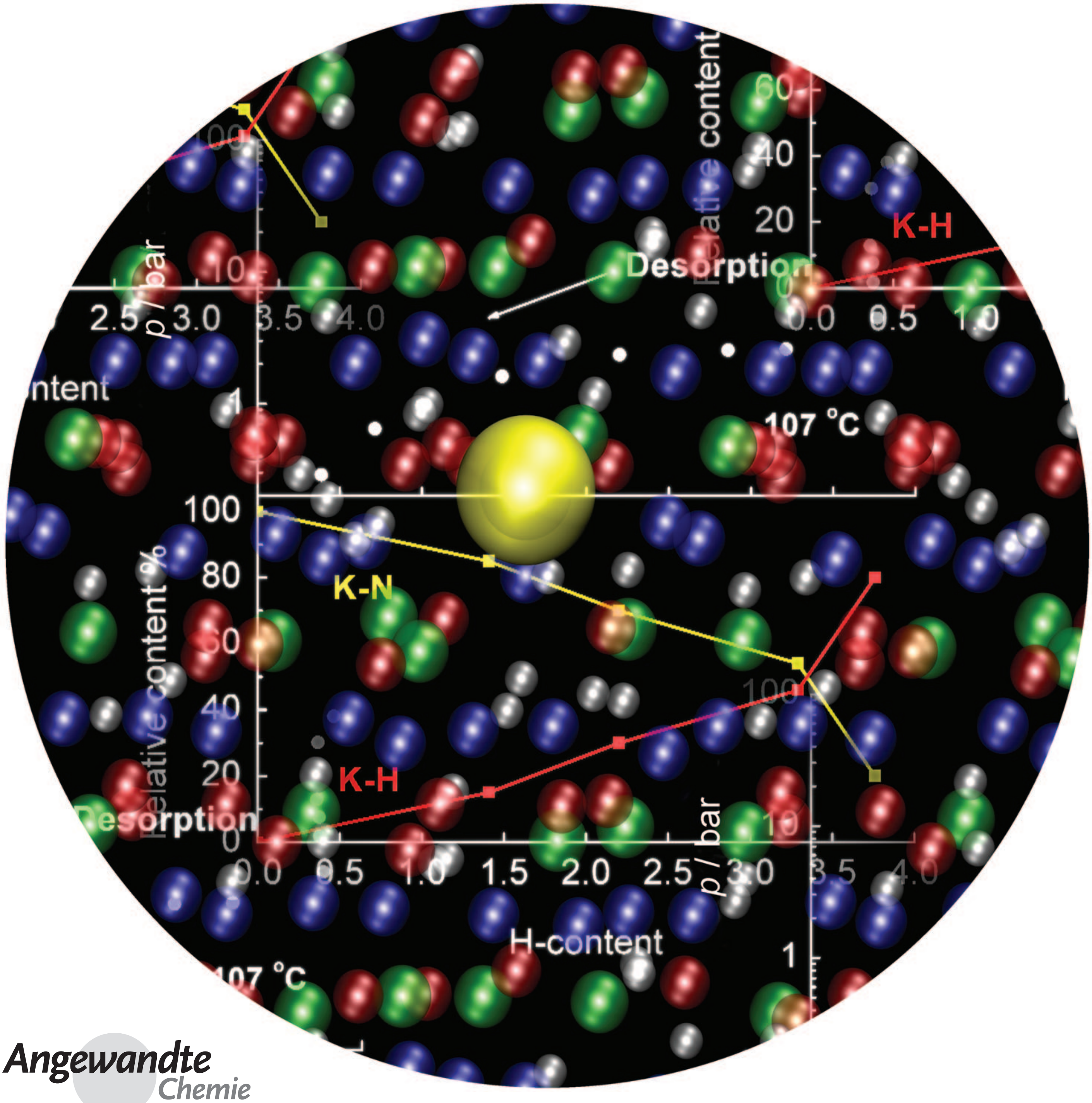

Hydrogen storage is one of the most challenging technical barriers in the implementation of hydrogen energy. To pursue highly efficient hydrogen storage systems, many complex hydrides with a high hydrogen content have been developed over the past decade.[1] However, most of those hydrides encounter serious kinetic problems upon hydrogen release. As an example, hydrogen desorption from $Mg(BH_4)_2$ is thermodynamically allowed at temperatures below 150 °C; however, temperatures above 250 °C are needed to overcome kinetic barriers.[2] Catalyzing heterogeneous solid-state reactions, such as dehydrogenation of $Mg(NH_2)_2/2\,LiH$ or $2\,LiBH_4/MgH_2$, appears to be more complicated than homogenous reactions, because the former usually involves stepwise phase and compositional changes.[3] Additives with catalytic potential have to be accommodated in the reaction region to be functional, which is difficult as the solubility of additive in a given lattice is confined by factors such as atomic/ionic size, crystal structure, electronegativity, and valence.[4] Herein, a new approach to promote the dehydrogenation of $Mg(NH_2)_2/2\,LiH$ is presented, which involves introducing a non-transition-metal dopant, potassium, into the reaction system. Experimental results show that complete hydrogen desorption can be carried out at circa 107 °C, which is substantially lower than that of the pristine system (i.e., >180 °C). Characterizations reveal that potassium diffuses into the imide and/or amide phases and combines with nitrogen. As a consequence, the amide N−H bonds and imide Li−N bonds are weakened, which considerably enhances the dehydrogenation.

The reversible hydrogen storage over the $Mg(NH_2)_2/2\,LiH$ system can be described by Equation (1). The system has a reversible hydrogen capacity of circa 5.6 wt. % and suitable thermodynamic parameters that allow the release of hydrogen at an equilibrium pressure of 1.0 bar at temperatures below 90 °C.[5] However, hydrogen release at an appropriate rate can only proceed at temperatures above 150 °C even if the $Mg(NH_2)_2/2\,LiH$ sample has been ball-milled intensively, which indicates the existence of a severe kinetic barrier. Mechanistic investigations indicated that the kinetic barrier may arise from the relocation of atoms across the amide/imide and imide/hydride phase boundaries, and from the mass transport along the product–imide layer.[6] Therefore, the potential catalyst has to be dissolved in the reaction region in order to be approachable by the reacting species. Our previous attempts to introduce conventional hydrogenation catalysts, such as Ti, Fe, Co, Ni, Pd, Pt, and/or their chlorides, could not bring much improvement to the system kinetics. It is likely that those additives cannot be effectively involved in the interfacial reactions and/or mass transport owing to poor solubility in amide, imide, or hydride.

$$\mathrm{Mg(NH_2)_2 + 2\,LiH \rightleftharpoons Li_2Mg(NH)_2 + 2\,H_2} \qquad (1)$$

Herein, potassium was selected because it can form a ternary amide with magnesium[7] and can be accommodated by imide (see below). The introduction of potassium was achieved by partially replacing LiH by KH. This potassium-modified system has the composition $Mg(NH_2)_2/1.9\,LiH/0.1\,KH$ (equivalent to 3 mol % KH in the sample). Figure 1 shows the temperature-programmed desorption (TPD) curves of H_2 and NH_3 from the pristine and the potassium-modified $Mg(NH_2)_2/2\,LiH$ samples. Relative to the pristine sample, the desorption peak of the potassium-modified sample shifts downwards by about 50 °C. The set-off temperature is remarkably reduced to circa 80 °C, which is the operation temperature of proton-exchange-membrane fuel cells. Moreover, NH_3, the side product, is hardly detectable in the potassium-modified sample in the temperature range of 75–200 °C. Similar performances can also be achieved by further reducing the potassium content from 3 mol % to 1 mol %.

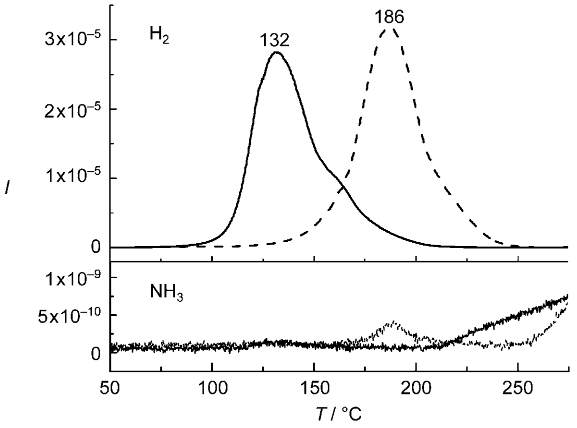

Figure 1. Temperature dependences of H_2 and NH_3 release from the potassium-modified (——) and the pristine samples (-----).

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Hydrogen desorption from $Mg(NH_2)_2/2\,LiH$ is actually a two-step process [Eq. (2),(3)].[8] Clearly, potassium can enhance the rates of both reactions and bring down the overall reaction temperature. Volumetric soak and release measurements at different temperatures also provide evidence for the significantly improved kinetics in the hydrogenation and dehydrogenation of the potassium-modified sample (see the Supporting Information). For example, about 75% of hydrogen can be absorbed by the potassium-modified sample at a low hydrogen pressure of 30 bar upon heating to 143 °C within 12 min. In contrast, it took more than 20 h for the pristine sample to reach the same level of hydrogenation.

$$2\,Mg(NH_2)_2 + 4\,LiH \rightleftharpoons Li_2Mg_2(NH)_3 + LiNH_2 + LiH + 3\,H_2 \qquad (2)$$

$$Li_2Mg_2(NH)_3 + LiNH_2 + LiH \rightleftharpoons 2\,Li_2Mg(NH)_2 + H_2 \qquad (3)$$

Full cycles of hydrogen uptake and release for the potassium-modified sample can be carried out at a temperature as low as 107 °C (Figure 2), which is the lowest temperature reported to date. In contrast, very little H_2 desorption from the post-milled fresh pristine sample was recorded at the same temperature owing to the severe kinetic barrier. The pressure–composition–temperature (PCT) isotherms of potassium-modified samples collected at 107 and 130 °C have a similar feature to that of the pristine sample recorded at 180 °C,[9] that is, desorption is composed of a plateau region and a sloping region. The H_2 pressure at the plateau region for the potassium-modified sample is more than 2.5 bar at 107 °C. From the van't Hoff plot (Figure 2 inset), the overall enthalpy change of hydrogen release is $42\,kJ\,mol^{-1}$ H_2 showing a slight change compared to the pristine sample.

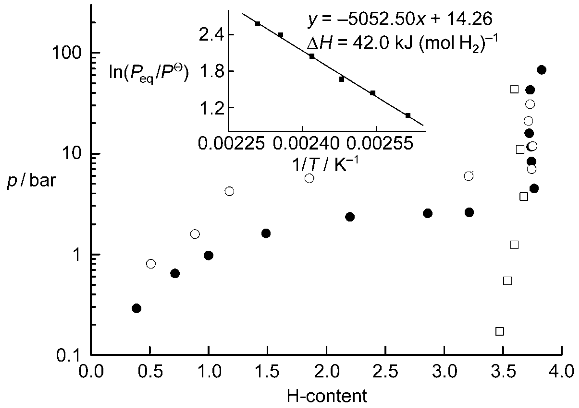

Figure 2. PCT desorption isotherms of the potassium-modified samples at 107 °C (●) and 130 °C (○), respectively, and the pristine sample at 107 °C (□). For the pristine sample, the dehydrogenation is too slow to reach equilibrium. Hydrogen content refers to the equivalent hydrogen atoms desorbed from the sorbent. Inset: van't Hoff plot of the potassium-modified sample.

To understand the role of KH, the potassium-modified samples collected at several stages of dehydrogenation and rehydrogenation were subjected to XRD characterization (see the Supporting Information). KH gradually disappeared upon dehydrogenation. The final product shows almost the same structure as that of the cubic ternary imide $Li_2Mg(NH)_2$,[9] but with poor crystallinity. During rehydrogenation, KH gradually reappeared, which indicates a reversible process. Direct observations of the local structure of potassium in the potassium-modified samples were obtained by employing X-ray absorption fine structure (XAFS) spectroscopy. As shown in Figure 3 a, the X-ray absorption near-edge structure (XANES) spectrum of potassium in the fully

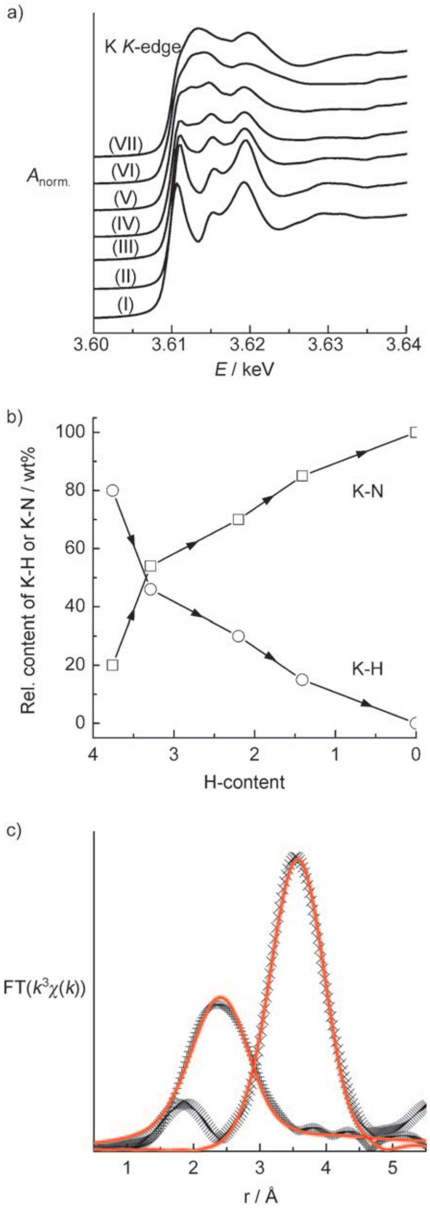

Figure 3. a) XANES transmission spectra at potassium K edge of KH (I), $K_2Mg(NH_2)_4$ (VII), and potassium-modified samples collected at different stages of dehydrogenation, with corresponding hydrogen content of 3.8 H (II), 3.3 H (III), 2.2 H (IV), 1.4 H (V), and 0 H (VI). b) Relative contents of the K–H (○) and K–N (□) components in the potassium-modified samples as a function of hydrogen content during dehydrogenation. c) Fourier transform of the EXAFS spectra of KH (×) and the fully dehydrogenated potassium-modified sample (+) and the fitted lines (in red). Phase shifts were not corrected.

hydrogenated sample (labeled II) has almost identical features as that of KH (I). As hydrogen release proceeded, the two peaks assigned to KH (ca. 3611 and 3619 eV) were gradually weakened, whereas a broad peak centered at about 3614 eV appeared and became the dominant peak upon full dehydrogenation (VI). Judging by the higher chemical shift in the absorption edge, potassium in the fully dehydrogenated sample should bond with the more electronegative element, namely nitrogen. As shown in Figure 3a, the overall features of $K_2Mg(NH_2)_4$ (VII) is similar to that of the dehydrogenated sample VI, confirming the formation of a K−N environment in VI. A reverse process can be observed upon the hydrogenation (see the Supporting Information). The relative content of the K−H and K−N components in the samples were estimated by fitting the corresponding XANES spectra with a linear combination, using KH (I) and the fully dehydrogenated sample (VI) as the references (see the Supporting Information). As shown in Figure 3b, the K−H component gradually transformed into the K−N component during the dehydrogenation. Interestingly, there is kickpoint at a hydrogen content of circa 3.5, showing a rapid enrichment of K−N content in the early stage of dehydrogenation, thus revealing that some of the KH reacts with $Mg(NH_2)_2$ to form the K−N species. Indeed, from the TPD curve (Figure 1) and the XANES spectra (Figure 3), a good correlation between the formation of K−N bonds and the enhanced hydrogen desorption kinetics can be observed. It is highly likely that the K−N component is the active species in promoting the dehydrogenation of $Mg(NH_2)_2/2\,LiH$.

The Fourier transform of the extended X-ray absorption fine structure (EXAFS) spectrum of the fully dehydrogenated potassium-modified sample is presented in Figure 3c. For comparison, the spectrum of KH is also shown. A clear K−K coordination at a radial distance of about 3.5 Å (4.0 Å after phase-shift correction) can be observed in KH, which corresponds to the second K−K shell in cubic KH. The first K−H shell in KH is unobservable (2.9 Å, theoretical bond length) because of the small scattering factor of hydrogen. In the fully dehydrogenated potassium-modified sample, only the K−N coordination of the first shell at circa 2.3 Å (2.9 Å after phase-shift correction) can be found. The absence of high-order K−K coordination peaks reveals the random dispersion of potassium in a lattice, showing the unlikelihood of the formation of an individual K−N-based phase of a given stoichiometry. By data fitting, the coordinate number N of potassium in the first coordination shell is 4.5, which is very close to that of Li−N (4) and Mg−N (4) in the $Li_2Mg(NH)_2$ structure (taken from Ref. [10]), showing that potassium ions in the fully dehydrogenated sample is probably hosted in the lattice of $Li_2Mg(NH)_2$ to form potassium-doped $Li_2Mg(NH)_2$. As pointed out by Rijssenbeek et al.,[10] the structure of $Li_2Mg(NH)_2$ is capable of accommodating large numbers of cation defects, which provides support to our XAFS results.

Although it is likely that potassium is accommodated by the imide phase, we can not rule out the possibility of formation of ternary amides/imides during the dehydrogenation, such as $K_2Mg(NH_2)_x(NH)_y$ with $(x,y)=(4,0)$, $(2,1)$, $(0,2)$[7] and $KLi_x(NH_2)_y$ with $(x,y)=(^1/_2,{}^3/_2)$, $(1,2)$, $(3,4)$, $(7,8)$,[11] and potassium-doped $Mg(NH_2)_2$. It is also possible that potassium somehow co-exists in both amide and imide phases to activate chemical bonding. As part of the generalized gradient approximation to density functional theory using the projector-augmented wave method, as implemented in the Vienna ab initio simulation package (VASP),[12] our preliminary simulation results show that when magnesium was partially replaced by potassium, the N−H bond in $Mg(NH_2)_2$ increases slightly in length from 1.026 Å to 1.029 Å. By replacing one lithium by potassium in the 112-atom superstructure $Li_{32}Mg_{16}(NH)_{32}$, the average distance between Li^+ and NH^{2-} increases from 2.202 Å to 2.218 Å. The weakened bonds will facilitate atom reallocation across the amide/imide and/or imide/hydride phase boundaries, and mass transport through the imide phase. As a consequence, much improved kinetics can be achieved. More details on the computational simulation work will be published in a separate publication.

It is noteworthy that similar performance can be achieved by introducing other potassium salts, such as KOH, KF, KNH_2, K_2CO_3, and K_3PO_4 to the $Mg(NH_2)_2/2\,LiH$ system. However, regardless of which additive was chosen, KH and the K−N-containing compound(s) are always the effective species.

In summary, remarkable enhancement in the kinetics of dehydrogenation is achieved by introducing potassium to the $Mg(NH_2)_2/2\,LiH$ system. In particular, reversible hydrogen release and uptake can be carried out at a temperature as low as 107 °C.

Experimental Section

Potassium-modified $Mg(NH_2)_2/2\,LiH$ was prepared by ball milling LiH (Fluka, 95%), $Mg(NH_2)_2$ (self-produced, $>95\%$) and KH (Fluka, mineral oil removed) in a molar ratio of 1.9:1.0:0.1 at 200 rpm on a Retsch planetary ball mill (PM400) for 36 h. The ball-to-sample weight ratio was about 60:1. The mixture was pretreated under vacuum to 130 °C for 40 h to release all hydrogen and then rehydrogenated with 80 bar H_2 to 100 °C for 40 h. The as-milled pristine sample of $Mg(NH_2)_2/2\,LiH$ (under the same ball milling conditions) was used directly for measurements. To prevent air contamination, sample handling was performed within a MBRAUN glovebox filled with purified argon.

Temperature-programmed desorption (TPD, with purified argon as carrier gas) was carried out on a system constructed in-house attached with an on-line mass spectrometer. H_2 and NH_3 signals were recorded at $m/z=2$ and 15, respectively. The heating rate was $2\,^{\circ}C\,min^{-1}$; samples of 100 mg were tested. Pressure–composition–temperature (PCT) isotherms were carried out on an automatic Sieverts-type apparatus (Advanced Materials Co.). A sample of circa 350 mg was used each time.

XAFS experiments at the potassium K-edge (3.608 keV) were performed in transmission mode at room temperature at XDD beamline in the Singapore Synchrotron Light Source (SSLS). Each sample was pressed into a pellet and placed in a helium-filled box sealed with Kapton windows on both sides for X-rays to pass through. The thickness of the samples was optimized to achieve a jump of about 0.6 at the absorption edge. Pure KH and the fully dehydrogenated sample of $1\,Mg(NH_2)_2/0.25\,KH$ from which $K_2Mg(NH_2)_4$ was developed were used as reference samples. The XAFS spectrum of KOH was also recorded (see the Supporting Information). Potassium K-edge XAFS spectra were analyzed by standard methods using the WINXAS code.[13] The extracted $\chi(k)$ values in the range 2.7–9.3 $Å^{-1}$ were weighted by k^3 and Fourier-transformed into R space using the

Bessel window function. Data fitting was performed in R space by filtering out the first and second coordination shells (1.1–4.5 Å). Theoretical backscattering amplitude and phase shift were extracted from cubic KH and KNH_2. Inelastic factor (S_0^2) was fixed to 0.9, which gives a reasonable result for the sample of pure KH. The effect of hydrogen atoms was not considered.

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[1] a) B. Bogdanović, M. Felderhoff, A. Pommerin, F. Schüth, N. Spielkamp, *Adv. Mater.* **2006**, *18*, 1198 – 1120; b) F. E. Pinkerton, M. S. Meyer, G. P. Meisner, M. P. Balogh, *J. Phys. Chem. B* **2006**, *110*, 7967 – 7974; c) K. Chłopek, C. Frommen, A. Léon, O. Zabara, M. Fichtner, *J. Mater. Chem.* **2007**, *17*, 3496 – 3503; d) P. Chen, Z. T. Xiong, J. Z. Luo, J. Y. Lin, K. L. Tan, *Nature* **2002**, *420*, 302 – 304; e) P. Chen, Z. T. Xiong, G. T. Wu, Y. F. Liu, J. J. Hu, W. F. Luo, *Scr. Mater.* **2007**, *56*, 817 – 822.

[2] T. Matsunaga, F. Buchter, P. Mauron, M. Bielman, Y. Nakamori, S. Orimo, N. Ohba, K. Miwa, S. Towata, A. Züttel, *J. Alloys Compd.* **2008**, *459*, 583 – 588.

[3] a) Z. T. Xiong, J. J. Hu, G. T. Wu, Y. F. Liu, P. Chen, *Catal. Today* **2007**, *120*, 287 – 291; b) W. Lohstroh, M. Fichtner, *J. Alloys Compd.* **2007**, *446–447*, 332 – 335.

[4] W. D. Callister, *Materials Science and Engineering: An Introduction*, 7th ed., Wiley, New York, **2006**, p. 84.

[5] Z. T. Xiong, J. J. Hu, G. T. Wu, P. Chen, W. F. Luo, K. Gross, J. Wang, *J. Alloys Compd.* **2005**, *398*, 235 – 239.

[6] P. Chen, Z. T. Xiong, L. F. Yang, G. T. Wu, W. F. Luo, *J. Phys. Chem. B* **2006**, *110*, 14221 – 14225.

[7] a) H. Jacobs, J. Birkenbeul, J. Kockelkorn, *J. Less-Common Met.* **1984**, *97*, 205 – 214; b) P. Palvadeau, J. Rouxel, *C. R. Seances Acad. Sci. Ser. C* **1968**, *266*, 1605 – 1607.

[8] J. J. Hu, Y. F. Liu, G. T. Wu, Z. T. Xiong, P. Chen, *J. Phys. Chem. C* **2007**, *111*, 18439 – 18443.

[9] Z. T. Xiong, G. T. Wu, J. J. Hu, P. Chen, *Adv. Mater.* **2004**, *16*, 1522 – 1525.

[10] J. Rijssenbeek, Y. Gao, J. Hanson, Q. Z. Huang, C. Jones, B. Toby, *J. Alloys Compd.* **2008**, *454*, 233 – 244.

[11] H. Jacobs, B. Harbrecht, *Z. anorg. Allg. Chem.* **1984**, *518*, 87 – 100.

[12] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169 – 11186.

[13] T. Ressler, *J. Physique IV* **1997**, *7*, 269 – 270.