

Insight into the hydrogenation properties of light weighted Laves phase materials $\text{CaLi}_{2-x}\text{Mg}_x$

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Summary

Metal hydrides are the only system capable of reversibly absorbing a large amount of hydrogen at ambient conditions [1]. Most of conventional metal hydrides are, however, composed of heavy transition and rare-earth metals resulting in low hydrogen capacity in weight (~3 mass%). To realize the hydrogen economy for transportation materials with more than 5 mass% of hydrogen capacity are required. This means light weighted metal alloys or compounds absorbing a similar amount of hydrogen as conventional metal hydrides should be developed. Although there exist several Laves phase AB_2 alloys based on light metal elements (Li, Mg, Al and Ca), only few studies about their hydrogenation properties have been reported [2-6]. This is probably because some of them do not absorb hydrogen at ambient conditions and others disproportionate into stable phases such as CaH_2 during hydrogenation. As mentioned earlier, since it would be difficult to avoid using those elements for developing new efficient hydrogen storage materials, it is important to elucidate mechanism behind disproportionation and find a way to prevent it. For these purposes, we propose detailed local and average structural studies on these materials using the atomic pair distribution function (PDF) [7] and Rietveld analysis.

key words:

Hydrogen storage materials, local structure, C14 Laves phase,

1. Objectives

$\text{CaLi}_{2-x}\text{Mg}_x$ is an excellent system to investigate for our purpose. CaLi_2 disproportionates into CaH_2 and LiH during hydrogenation but the partial substitution of Mg for Li seems to make a more robust C14 Laves phase structure against disproportionation [3]. We are specifically interested in

1. $\text{CaLi}_{2-x}\text{Mg}_x$ hydride samples show broad intensities underneath Bragg peaks in X-ray diffraction patterns. What is the origin of newly appeared intensities?
2. Hydrogenation of $\text{CaLi}_{2-x}\text{Mg}_x$ leads to the lattice contraction. Why?
3. What is the role of Mg in a more robust metal frame against disproportionation?

To answer these questions we need to investigate not only the average but also the local structure of these materials. Broad intensities under the Bragg peaks are impossible to analyze with conventional crystallography and information of local atomic bonding is important to understand the lattice contraction. In this study we will employ the PDF analysis, a powerful local structural probing tool for amorphous and nano-materials. Successfully identifying the

nature and the origin of newly developed broad intensities and the unusual lattice contraction found in hydrogenated $\text{CaLi}_{2-x}\text{Mg}_x$ will elucidate the role of Mg in an enhanced structure against disproportionation and consequently lead us to an idea to improve hydrogen storage properties of $\text{CaLi}_{2-x}\text{Mg}_x$.

2. Methods

$\text{CaLi}_{2-x}\text{Mg}_x$ ($x=0.5$ and 1) were prepared by induction melting. Hydrogenation was done at 283 K. A half of the hydride powder sample was kept at below 283 K ($\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT and $\text{CaLiMgH}_{-1.5}$ -LT) and the other half was kept at room temperature ($\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -RT and $\text{CaLiMgH}_{-1.5}$ -RT). X-ray total scattering experiments were carried out at BL14B1 at SPring-8. Powder samples of $\text{CaLi}_{2-x}\text{Mg}_x$ ($x=0.5$ and 1) alloy and hydride were packed with kapton tapes and placed in a square shaped sample holder made of Cu. The sample holder was mounted on a κ -type multi-axis diffractometer coupled with a NaI scintillation detector and shielded with Be windows. Each sample was cooled down to 263 K using a closed-cycle He gas refrigerator and total scattering data were collected with an incident X-ray energy of 60.2684 keV ($\lambda=0.205720$ Å). The signal from an empty container (a kapton tape) was subtracted from the raw data, and various other corrections were made [7]. The X-ray PDFs were obtained using the program PDFgetX2 [8]. For local structural studies the PDFgui program [9] was used for real space modeling.

3. Results and Discussion

Because $\text{CaLi}_{2-x}\text{Mg}_x$ and $\text{CaLi}_{2-x}\text{Mg}_x\text{H}_y$ are composed of relatively light elements, Q_{\max} (Q =momentum transfer= $4\pi\sin(2\theta/2)/\lambda$ [7]) used for obtaining the PDF was 15 \AA^{-1} .

Hydride samples of $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ showed broad intensities under the C14 peaks in diffraction patterns. Keeping $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ at room temperature leads to increase in broad intensities and broadening of C14 diffraction peaks. This suggests that the C14 structure becomes heavily disordered or possibly becomes amorphous by hydrogenation. However, $\text{CaLiMgH}_{-1.5}$ does not show such readily visible broad intensities in diffraction patterns.

In Figure 1, the X-ray PDFs of $\text{CaLi}_{1.5}\text{Mg}_{0.5}$, $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT and $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -RT are plotted over a wide- r range. Well crystallized nature of $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ can be seen from sharp PDF peaks continuing up to high- r regions (Figure 1). However, the PDF peaks of $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT get broadened and overall profile becomes smaller. This tendency is greater in $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -RT PDF; PDF peaks decay quickly with r and there is almost no signal in high- r regions. PDF refinements were carried out using the average C14 structural model. The representative PDF fits of $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT and $\text{CaLiMgH}_{-1.5}$ -LT are shown in Figure 2(a) and (b), respectively and refined lattice parameters are given in Table 1. The lattice contraction of hydride samples can be clearly seen. Around 4.8% and 2% of the unit cell volume was reduced in $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ and CaLiMg respectively, after hydrogenation. For both cases, PDF peaks below 20 Å are well explained by the average C14 structure. Interestingly, no apparent amorphous like signal was found in the difference curve of $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT. Instead, relatively large values of isotropic atomic displacement parameters (U_{iso}) for Li (0.1333 \AA^2) and Ca (0.0318 \AA^2) were needed to obtain good fits. Much larger values of U_{iso} were obtained from $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ -RT, which shows more growth of broad intensities in diffraction patterns than $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_{-3}$ -LT. These PDF refinement results imply the heavily disordered nature of the structure. Further analysis is underway and a neutron total scattering experiment is planned for obtaining

complementary information.

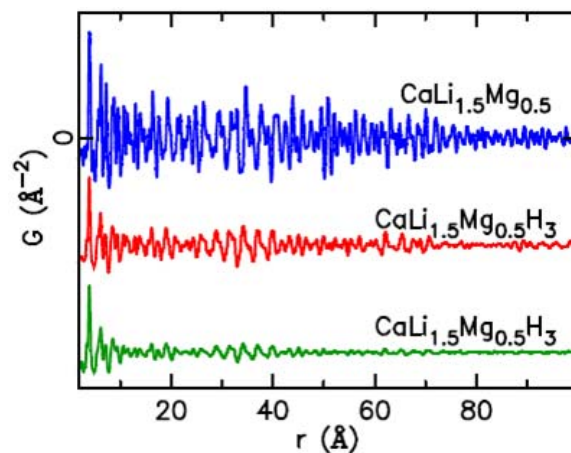


Figure 1. X-ray PDFs of $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ (blue), $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_3$ -LT (red) and $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_3$ -RT (green).

Table 1. Lattice parameters obtained from PDF refinements.

	$\text{CaLi}_{1.5}\text{Mg}_{0.5}$		CaLiMg	
	a	c	a	c
alloy	6.232	10.144	6.212	10.122
hydride kept at LT	6.133	9.968	6.182	10.014
hydride kept at RT	6.131	9.993	6.194	10.079

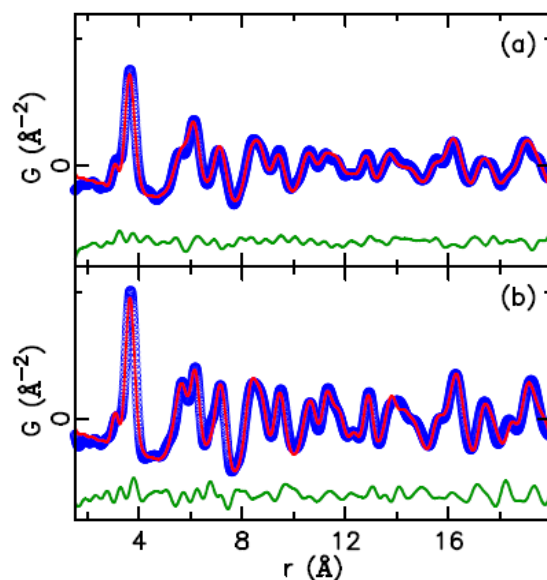


Figure 2. PDF refinement results of (a) $\text{CaLi}_{1.5}\text{Mg}_{0.5}\text{H}_3$ -LT and (b) $\text{CaLiMgH}_{1.5}$ -LT using the C14 Laves phase structural model. Data and calculation using the model are in blue open circles and red lines, respectively. Difference between data and model is offset.

4. References

- [1] L. Schlapbach and A. Züttel, *Nature* 414, 353-358 (2001).
- [2] X. Liu et al., *Int. J. Hydrogen Energy* 34,1472-1475 (2009).
- [3] K. Asano et al., *J. Alloys. Compd.* 482, L18-L21 (2009).
- [4] N. Terashita and E. Akiba, *Mater. Trans.* 45, 2594-2597 (2004).
- [5] H. Tanaka et al., *J. Alloys. Compd.* 231, 675-678 (1995).
- [6] Q. A. Zhang et al., *Mater. Chem. Phys.* 104, 373-376 (2007).
- [7] T. Egami and S. J. L. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials*, Pergamon Press Elsevier, Oxford, England, 2003.
- [8] Qiu, X.; Thompson, J. W.; Billinge, S. J. L. *J. Appl. Crystallogr.* **37**, 678 (2004).
- [9] Farrow, C. L.; Juhas, P.; Liu, J. W.; Bryndin, D.; Božin, E. S.; Bloch, J.; Proffen, Th.; Billinge, S. J. L. *J. Phys.: Condens. Matter* **19**, 335219 (2007).