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Unusual Volume Reduction in $\text{CaLi}_{2-x}\text{Mg}_x$ by Hydrogen Uptake

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Abstract

To understand the hydrogen storage properties of $\text{CaLi}_{2-x}\text{Mg}_x$ having a C14 Laves phase structure, changes in its average and local structures by hydrogenation were investigated by using the Rietveld and the atomic pair distribution function analyses of X-ray diffraction data. We found that after hydrogen uptake at 283 K, Mg-containing samples exhibit a C14 phase with reduced volume. This C14 phase readily decomposes into CaH_2 at temperatures higher than 300 K. Our study suggests that hydrogen absorption in $\text{CaLi}_{2-x}\text{Mg}_x$ at 283 K is multi-step reaction. Lithium that can easily diffuse through C14 crystals reacts with hydrogen forming a Li-rich hydride phase. On the other hand, slow diffusion of large Ca atoms and strong Mg-Mg and Mg-Ca interaction restrain the immediate formation of CaH_2 . As a result, there is a substantial time lag between the formation of a Li-rich hydride phase and the formation of CaH_2 at 283 K. This brings about a C14 phase with reduced volume where a large number of Li vacancies are present immediately after hydrogenation.

Keywords: C14 Laves phase, hydrogen absorbing materials, X-ray diffraction, atomic pair distribution function

Background and Purpose

It has been reported that Li-rich $\text{CaLi}_{2-x}\text{Mg}_x$ ($x>0$) having a C14 Laves phase structure, a hexagonal MgZn_2 -type structure ($P6_3/mmc$ space group), absorbs hydrogen at ambient temperature without altering a crystal structure type [1]. These hydrogen absorption properties are unusual since AB_2 Laves phase materials composed solely of light metals, such as Ca, Mg and/or Al, typically require temperatures higher than 473 K to react with hydrogen and easily decompose into CaH_2 , Mg and/or Al during hydrogen uptake [2]. Despite of these interesting properties, a detailed structural study on $\text{CaLi}_{2-x}\text{Mg}_x$ has not been conducted. In this study, we conduct a thorough structural study of $\text{CaLi}_{2-x}\text{Mg}_x$ using Rietveld and atomic pair distribution function (PDF) analyses of Synchrotron X-ray total scattering data.

Experimental Summary

Pressure-composition isotherm (PCT) measurement of $\text{CaLi}_{2-x}\text{Mg}_x$, $x=0, 0.5$, and 1 was carried out at 248 K for CaLi_2 and 283 K for $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ and CaLiMg . Synchrotron X-ray total scattering experiments were carried out at BL22XU [3] and BL14B1 [4] beamlines at SPring-8. For the experiment at BL22XU, fine powder samples of CaLi_2 , $\text{CaLi}_{1.5}\text{Mg}_{0.5}$, CaLiMg and hydrogenated CaLiMg kept at room temperature for more than three years were loaded in kapton capillaries with a diameter of 1.0 mm. Data were collected at room temperature with a large image plate (IP) detector, R-Axis V manufactured by Rigaku [3]. The incident X-ray beam of 70.16 keV ($\lambda=0.1768$ Å) and 70.430 keV ($\lambda=0.17604$ Å) were used. For the experiment at BL14B1, a fine powder sample of hydrogenated CaLiMg kept at 282 K for a week and that kept at room temperature for a week were loaded between kapton tapes and placed in a square-shaped sample holder made of copper. The sample holder was mounted on a κ -type multi-axis diffractometer coupled with a NaI scintillation detector and shielded with beryllium windows [4]. Each sample was cooled down to 263 K using a closed-cycle helium gas refrigerator and total scattering data were collected with an incident X-ray energy of 60.2684 keV ($\lambda=0.205720$ Å). The PDFgetX2 program [5] was used for processing the X-ray PDFs. Structural modeling in reciprocal space was carried out by the Rietveld method using the RIETAN-FP program [6]. For local structural studies, the PDFgui program [7] was used for real space modeling.

Results and Discussion

PCT measurement shows that CaLi_2 absorbs H/M (the number ratio of hydrogen to metal atoms) ~ 1.2 of hydrogen. This corresponds to ~ 6.7 mass% of hydrogen. The amount of absorbed hydrogen by

$\text{CaLi}_{1.5}\text{Mg}_{0.5}$ is H/M~1 (~4.8 mass%) and that by CaLiMg is H/M~0.5 (~2.1 mass%).

Rietveld analysis results using synchrotron X-ray total scattering data show that main diffraction peaks of $\text{CaLi}_{2-x}\text{Mg}_x$, $x=0, 0.5$ data are well explained by a C14 Laves phase structural model. The refined lattice parameters are $a=6.2709(7)$ Å and $c=10.232(1)$ Å for CaLi_2 , $a=6.2463(6)$ Å and $c=10.1947(9)$ Å for $\text{CaLi}_{1.5}\text{Mg}_{0.5}$, and $a=6.2361(5)$ Å and $c=10.1916(9)$ Å for CaLiMg . The C14 structural model also explains the overall features of the X-ray PDFs of $\text{CaLi}_{2-x}\text{Mg}_x$ below 20 Å indicating that the local structure does not deviate significantly from the average structure.

X-ray diffraction patterns of CaLi_2 after PCT measurement obtained using $\text{Cu } K_\alpha$ radiation show diffraction peaks of CaH_2 and LiH indicating that CaLi_2 is decomposed by hydrogenation. Meanwhile, $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ after hydrogenation does not show neither CaH_2 nor LiH diffraction peaks. Instead, small diffraction peaks of a C14 Laves phase were observed (Fig. 1(a)). Compared to the diffraction lines before hydrogenation, these peaks all shift to higher 2θ . This is somewhat peculiar since hydrogen uptake usually leads to appreciable volume expansion in conventional metals, metal alloys and intermetallic compounds often accompanying change in structure types. When the structure type remains unchanged, volume expansion emerges as a considerable shift of diffraction peaks to lower 2θ . However, peak shifts seen in Fig. 1(a) occur in the opposite direction indicating the shrinkage of the C14 lattice. Moreover, there is a very broad hump underneath these diffraction peaks. In fact, we noticed that the hydrogenated $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ sample is composed of silvery particles and gray particles. Although difficult, it is not impossible to separate the gray particles from the silvery ones. The gray particles were pulverized without difficulty. The X-ray diffraction pattern of gray powder (a green line in Fig. 1(a)) coincides well with the broad hump found underneath the diffraction peaks after hydrogenation. This strongly suggests that during hydrogen uptake some of metal atoms are dissociated from the C14 crystals and involved in the formation of an amorphous-like phase. CaLiMg , a Mg-rich sample, also displays unusual volume reduction (Fig. 1(b)). However, there are several characteristics distinct from $\text{CaLi}_{1.5}\text{Mg}_{0.5}$. First of all, even after hydrogenation the diffraction peaks remain relatively sharp. Some of the peaks show a drastic diminution in intensity. In addition, no distinct broad hump underneath the diffraction peaks of a C14 phase is present and no sign of CaH_2 or LiH is seen. Furthermore, peak shifts in CaLiMg are much smaller than those in $\text{CaLi}_{1.5}\text{Mg}_{0.5}$. Volume reduction is roughly assessed at 6.4 % for $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ and 2.1 % for CaLiMg . Note that the extent of a peak shift varies from peak to peak indicating that there is a certain direction along which lattice contraction takes place predominantly. In fact, for both samples, the c -axis lattice parameter decreases (-2.7 % for $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ and -1.0 % for CaLiMg) more than the a - or b -axis lattice parameter (-2.0 % for $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ and -0.6 % for CaLiMg).

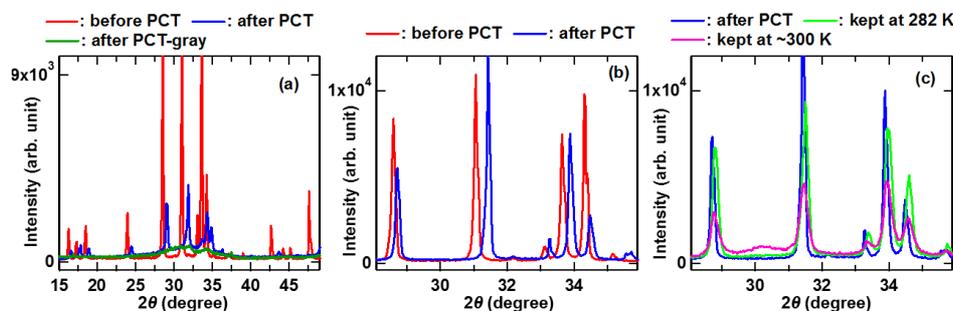


Fig. 1. X-ray diffraction patterns of (a) $\text{CaLi}_{1.5}\text{Mg}_{0.5}$ (b) CaLiMg before and after PCT measurement using $\text{Cu } K_\alpha$ radiation. (c) X-ray diffraction patterns of hydrogenated CaLiMg kept at 282 K and 300 K are shown.

The results so far reveal an interesting correlation. A sample with a *higher* lithium content absorbs *more* hydrogen and shows *greater* volume reduction. The atomic fraction of calcium is equal for all the samples and both the amount of absorbed hydrogen and the extent of volume reduction decrease with increasing the magnesium content. Therefore, lithium seems to play a critical role in hydrogen uptake in $\text{CaLi}_{2-x}\text{Mg}_x$. It is most reasonable to conclude that when $\text{CaLi}_{2-x}\text{Mg}_x$ ($x>0$) reacts with hydrogen, some of Li atoms are freed from the C14 crystals forming a Li-rich hydride phase like LiH or Li-rich Li-X-H ($X = \text{Ca}$ or/and Mg). However, owing to low experimental temperature (283 K), the structural correlation of the Li-rich hydride phase is not well defined consequently leading to an amorphous-like broad diffraction pattern as clearly seen in Fig. 1(a). The removal of lithium from $\text{CaLi}_{2-x}\text{Mg}_x$ leaves vacancies in the lattice and these vacancies should contribute greatly to the unusual volume reduction of the C14 phase. Since peak shifts found in Fig. 1(a) and (b) are large, a fair number of vacancies should be formed. Furthermore, to have

such apparent diffraction peaks C14 structural characteristics should remain to a certain degree in the presence of a large number of vacancies. Our first principles calculations show that one Li vacancy in a unit cell induces similar diffraction peak shifts as the experimental data indicating that C14 structural characteristics can remain.

To study the stability of the C14 phase remaining after hydrogen uptake (henceforth, we call it a hydrogenated C14 phase) we kept hydrogenated CaLiMg at two different temperatures, 282 K (CaLiMg-H-282 K) and 300 K (CaLiMg-H-300 K), in an argon atmosphere for a week and examined changes in their structures. The sample kept at 282 K exhibits little broadened yet still intense C14 diffraction peaks (Fig. 1(c)). No apparent new peaks appear. However, a slight increase in temperature to 300 K triggers considerable changes (a magenta line in Fig. 1(c)). Diffraction peaks get more broadened than those of CaLiMg-H-282 K, and peak intensities significantly diminish. Moreover, a new broad peak emerges at $2\theta \approx 30^\circ$ compensating for the loss of C14 diffraction peak intensity. These results strongly suggest that the hydrogenated C14 phase is unstable at 300 K and easily decomposes.

To further investigate changes in the hydrogenated C14 phase at 300 K, we obtained the synchrotron X-ray PDFs of CaLiMg-H-282 K and CaLiMg-H-300 K. A C14 structural model that does not contain hydrogen atoms was refined until the best agreement to the experimental PDF data was obtained, and then features that were not explained by the model were examined. PDF fitting results are shown in Fig. 2(a)-(c). Although it is not entirely satisfactory, the model reproduces the overall PDF profile of CaLiMg-H-282 K to a reasonable degree (Fig. 2(a)). For the case of CaLiMg-H-300 K, however, disagreement between the data and the model is apparent; not only peak intensities but also the positions and shapes of some peaks are poorly explained (Fig. 2(b)). As shown in Fig. 2(c), a much worse fit was obtained for the sample kept at 300 K for more than three years indicating that this change is extremely slow and not complete in a week. Interestingly, we found that the difference curves in Fig. 2(a)-(c) contain information about the development of CaH₂ structural correlation. In Fig. 2(d)-(f), the difference curves obtained in Fig. 2(a)-(c) are compared to the calculated CaH₂ PDF. For the difference curve of CaLiMg-H-282 K (Fig. 2(d)), a sharp feature at $\sim 3.8 \text{ \AA}$ is aligned with the first PDF peak of CaH₂ and there is a hint of CaH₂-like features in $4 < r < 9 \text{ \AA}$. However, features in $r > 9 \text{ \AA}$ do not match those of CaH₂. This is similar to the case of an amorphous PDF, where a sharp first peak is followed by two or three broad peaks reflecting the presence of short-range structural order. This indicates that CaH₂ structural correlation in CaLiMg-H-282 K is poorly developed at this stage. For the difference curve of CaLiMg-H-300K (Fig. 2(e)), intensity fluctuation in $r < \sim 14 \text{ \AA}$ resembles the CaH₂ PDF indicating the development of short-to-medium range structural order of CaH₂. As time passes, the CaH₂ structural correlation becomes more apparent and extends over a much longer- r range (Fig. 2(f)). Therefore, the new broad peak appearing at $2\theta \approx 30^\circ$ in Fig. 1(c) is from CaH₂. These PDF results clearly demonstrate that the hydrogenated C14 phase easily decomposes into CaH₂ at 300 K.

Making use of the results obtained, we are able to understand the hydrogen absorption process in CaLi_{2-x}Mg_x to some extent. A sample with a high lithium content absorbs a larger amount of hydrogen, undergoes a greater volume reduction, and exhibits a more intense amorphous-like background than one with a low lithium content. This strongly suggests that during hydrogen uptake some of Li atoms pulled out of the crystals resulting in unusual hydrogenation-induced volume reduction. According to the theoretical study of Ref. [8], the structural stability of CaLi_{2-x}Mg_x increases with the magnesium content owing to strong Mg-Mg and Mg-Ca bonds. Probably these strong Mg-Mg and Mg-Ca bonds limit the dissociation of Li preventing the C14 crystals from completely collapsing.

Change in the hydrogenated C14 phase at 300 K provides us more information. As seen in Fig. 1(c), the arising of a CaH₂ peak and the decreasing of C14 peak intensities occur *concurrently*. This indicates that Ca atoms are easily dissociated from the hydrogenated C14 phase at 300 K. Hydrogen was probably dragged from the Li-rich hydride phase to form CaH₂. Alternatively, the hydrogenated C14 phase might contain some hydrogen. Then, what is the reason that CaH₂ did not form in the first place despite of its high stability (the formation enthalpy of CaH₂, LiH, and MgH₂ are -174.5, -157.3, and -74.5 kJ/mol H₂, respectively [9])? This is because of the slow diffusion of large Ca atoms at 283 K. Chemical frustration of large atoms at low temperatures often leads to the formation of a single amorphous hydride phase [10]. In our case, however, the presence of lithium yields a totally different outcome. Small Li atoms can easily diffuse through crystals even at 283 K. This ability of lithium allows CaLi_{2-x}Mg_x to react with hydrogen at ambient conditions. Note that CaMg₂, lithium-free composition, does not absorb hydrogen at ambient conditions [2]. On the other hand, slow Ca diffusion and strong Mg-Mg and Mg-Ca interaction work together to obstruct the immediate formation of CaH₂. Consequently, only Li atoms are freed from C14 crystals forming a Li-rich amorphous-like hydride phase and leaving a Li-poor C14 phase behind.

Numerous vacant sites resulting from the removal of lithium allow large Ca atoms to migrate more easily. This is the reason why CaH_2 can be easily formed when the hydrogenated C14 phase is exposed to slightly higher temperatures than 283 K. In fact, the formation of CaH_2 was also observed in the hydrogenated CaLiMg sample kept at 282 K for a long period of time indicating that the diffusion of Ca atoms is extremely slow at 282 K.

As we have discussed so far, the hydriding process of $\text{CaLi}_{2-x}\text{Mg}_x$ ($x > 0$) at 283 K is at least two-step process; a Li-rich hydride phase forms first and then the formation of CaH_2 takes place over a long period of time. As a result, there is a substantial time lag between the formation of a Li-rich hydride phase and the formation of CaH_2 at 283 K. This brings about a C14 phase with reduced volume where a large number of Li vacancies are present immediately after hydrogenation. At temperatures higher than 300 K, however, these two seem to occur almost simultaneously. In the earlier study, volume reduction by hydrogen uptake was not reported [1]. Although $\text{CaLi}_{2-x}\text{Mg}_x$ was hydrogenated at two different temperatures, 283 K and 313 K, in Ref. [1], it was not mentioned which temperature X-ray diffraction patterns correspond to. We speculate that the diffraction patterns correspond to the samples hydrogenated at 313 K because all of them display a CaH_2 peak. Hence, $\text{CaLi}_{2-x}\text{Mg}_x$ directly decomposed into LiH and CaH_2 and the unreacted part of the sample gave rise to the diffraction peaks of a C14 phase with no volume reduction.

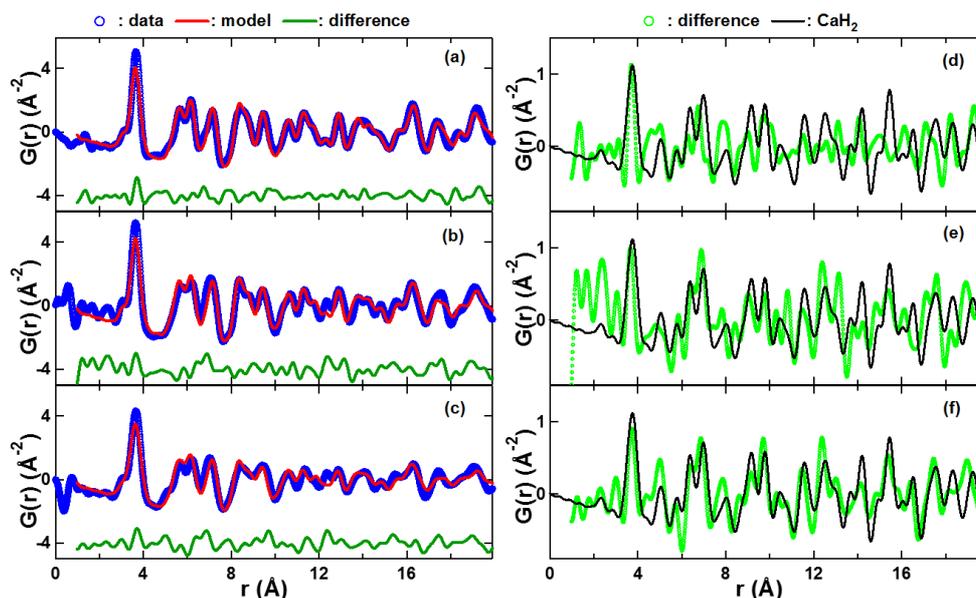


Fig. 2. PDF refinement results. The experimental X-ray PDFs of (a) CaLiMg-H-282 K, (b) CaLiMg-H-300 K, and (c) the hydrogenated CaLiMg sample kept at 300 K for more than three years are plotted with calculated PDFs using refined C14 structural models. Difference between the experimental and calculated PDFs is plotted below the data in each panel for clarity. Difference curves obtained from PDF modeling using data of (d) CaLiMg-H-282 K, (e) CaLiMg-H-300 K, and (f) the hydrogenated CaLiMg sample kept at 300 K for more than three years are compared to the calculated PDF of CaH_2 .

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