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Structural study of a new B-rich phase obtained by partial hydrogenation of $2NaH + MgB_2$

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Abstract

The structure of an unknown crystalline phase observed during the hydrogen absorption reaction of the powder mixtures 2NaH þ MgB_2 at high pressure has been studied by ab-initio structure determination from powder diffraction. The sequence of un-overlapped peaks extracted from the X-ray powder diffraction pattern could be indexed with a prim-itive cubic cell with lattice parameter a ¼ 7.319 A˚. The diffraction patterns of the peaks are matched with the Pa-3 space group. The stoichiometry of the hydrogen absorption reaction suggests the presence of a high-boron content phase in the compound under investigation. Assuming this phase to be composed only by boron atoms and therefore having a density similar to that found for boron polymorphs, the solution with a space group of Pa-3 leads to reasonable BeB interatomic distances.

1. Introduction

Light metal borohydrides, e.g. $LiBH_4$, $NaBH_4$ containing up to 18 wt% of H_2, are considered as promising candidates for H_2 storage. However, high thermodynamic stability and poor reversibility are important issues to be addressed before considering them as suitable energy carrier for vehicular and stationary applications [1]. In order to overcome these ther-modynamic constrains, the Reactive Hydride Composite (RHC) concept was developed [2e4]. This method allows accessing favorable reaction enthalpy while maintaining a high gravimetric hydrogen capacity. The approach by Reilly and Wiswall [5], which used reactive additives to facilitate hydrogen release at milder conditions, has been recently modified by using another hydride as additive to tune the thermodynamic properties of hydrogen storage materials while maintaining a high gravimetric hydrogen storage den-sity [6]. Systems to which this approach applies amongst others are $2NaBH_4$ þ MgH_2, $2LiBH_4$ þ MgH_2 and $Ca(BH_4)_2$ þ MgH_2 [4]. In spite of the possibility to use selected hydride mixtures for tuning the thermodynamic properties of boro-hydrides, the issue of limited reversibility still remains a pri-mary challenge associated with this class of materials. This limitation is mostly due to kinetic barriers and to the formation of stable intermediate phases and side products. Recently, the sorption properties of the system 2NaH þ MgB_2 and of its reaction products were deeply investigated by several authors [7e17]. This mixture is considered a model system for studying the hydrogen sorption properties of reactive hydride composites based on MgB_2. In a previous publication [12], we described the effect of the applied hydrogen pressure on the absorption reaction mechanism of the system 2NaH þ MgB_2 [12]. As a main result, it was observed that the reaction path strongly depends on the applied hydrogen pressure. At 50 and 25 bar, the formation of $NaBH_4$ was preceded by the formation of unidentified B-containing crystalline phases and $NaMgH_3$; whereas under a hydrogen pressure of 5 bar led to the direct formation of $NaBH_4$. The study of this unknown phase is of extreme interest. In fact, according to the magic angle spinning nuclear magnetic resonance (MAS NMR) analyses performed on partially hy-drogenated material this phase contains hydrogen. Moreover, its temperature of formation and melting are much lower than those observed for $NaBH_4$ [12]. In order to give a struc-tural description of the unknown crystalline phase, a careful analysis of powder X-ray diffraction data (PXRD) is required.

The ability to solve the crystalline structure of unknown compounds directly from powder XRD patterns is needed in all the cases, when the synthesis of single crystal of the analyzed compound cannot be achieved; and appears partic-ularly useful in the context of new phases created after hydrogen treatment. In fact, it is now possible to solve the powder patterns “ab-initio”, i.e., based only on an estimate of the chemical composition of the system under investigation. Recently, this approach has attracted considerable attention [18], in the fields of both pharmaceutical compounds [19], and material science [20e23]. The availability of numerical soft-ware [24,25] that accompanied the instrumental development in terms of high-temperature and high-pressure “in situ” measurements at synchrotron radiation facilities has strongly contributed to the application of this approach for crystalline structure determination.

In the present work, we attempt to determine the crystal structure of an unknown phase observed to precede the for-mation of $NaMgH_3$ and $NaBH_4$ during the hydrogen absorption reaction performed at 50 bar of hydrogen pressure in the 2NaH þ MgB_2 system. The PXRD patterns used to solve the crystal structure of the unknown phase are rather complex. In fact, the patterns consist of a series of diffraction peaks belonging to reagent and product phases, together with extra un-indexed peaks related to the unknown intermediate phase. Thus, the solution of an unknown phase represents a challenging application of the “ab-initio” approach. A considerable effort in this work stands on the separation of the diffraction peaks of the unknown crystalline phase from the whole complex pattern by using the Rietveld method. From the subtracted pattern, the crystal structure of a high-boron containing phase has been determined.

2. Experimental

NaH (95% purity) and MgB_2 (99.99% purity) were purchased from SigmaeAldrich and Alfa Aesar, respectively. NaH and the MgB_2 in the molar ratio 2:1 were charged into a hardened steel vial and milled for 1 h in a Spex 8000 ball mill, with a ball-to-powder ratio of 10:1. Handling and milling were performed in a dedicated glove box under a continuously purified argon atmosphere. The hydrogenation of the material was per-formed in a PCTPro-2000 (SETARAM Instruments). Separate batches of partially hydrogenated mixtures have been pre-pared and used for the PXRD analysis.

PXRD investigations were carried out at the Helmholtz-Zentrum Geesthacht (HZG) (Germany) using a Siemens D5000 diffractometer in reflection geometry and at the Chemistry Department of University of Turin (UNITO) (Italy) with a PANalytical instrument in transmission geometry, respectively. Cu Ka radiation has been used in both cases. While in the first equipment the sample holder is a glass cir-cular cavity of 0.1 mm in depth with area 1.5 cm^2, containing ca. 100 mg of powder, in the second system the sample holder is a capillary. In both cases the instrumental functions were determined using a LaB_6 standard. The patterns were collected in the range from 15 to 90 in 2q with a step size of 0.025 , using a multidetector in the diffracted beam. The overall data collection lasted ca. 6 h, implying that for each step the counting is accumulated for 7.2 s. The comparison of the two patterns aims from one hand to assess the nature of products after the two synthesis reactions conducted under extreme conditions (kinetics reproducibility). On the other hand the DebyeeScherrer like configuration using a capillary as sample holder should ensure a high reliability of the 2q-scale of the pattern, i.e. absence of zero shift, and a powder preserved from oxidation phenomena during the measurement.

3. Results and discussion

Several attempts to maximize the formation of the unknown phase over the starting reactants $NaBH_4$ and $NaMgH_3$ were made by changing the hydrogenation parameters. It was found that the formation of the unknown phase was maxi-mized by heating the sample up to 310 C under 50 bar of hydrogen pressure with a heating rate of 20 C/min, then rapidly cooling down to cryogenic temperature using liquid nitrogen.

The PXRD patterns of the partially hydrogenated 2NaH þ MgB_2 mixtures collected at the HZG and at the UNITO are reported in Fig. 1.The patterns are expressed as a function of the reciprocal space variable Q ¼ 4psin q/l. From the PXRD analysis performed by the two laboratories, it turns out that the phase mixture obtained after the hydrogen absorption process of the 2NaH þ MgB_2 is rather close for both batches. From a visual inspection of PXRD patterns, it can be noticed that the partially absorbed sample analyzed at HZG shows an amount of NaH smaller than that observed in the pattern ac-quired at UNITO. This suggests a higher conversion of the starting reactants into the hydrogenated products for the material analyzed at HZG. Other minor differences are observed in the peak-to-background ratio. This may be attributed to differences in specimen preparation and/or to differences in the counting resolution system employed in the two laboratories.

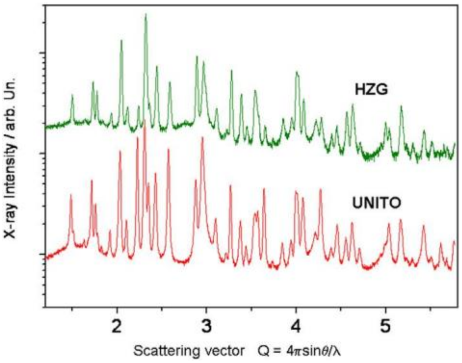

Fig. 1 e PXRD pattern of the partially hydrogenated 2NaH D MgB_2. HZG [PXRD pattern collected at the Helmholtz-Zentrum Geesthacht; UNITO [PXRD pattern collected at the University of Turin.

Among the phases present in the two analyzed samples, the Bragg reflections of starting reactants NaH (cubic, S.G. Fm-3m) and MgB_2 (hexagonal, S.G. P6/mmm) are visible together with the hydrogenation products $NaMgH_3$ (orthorhombic, S.G. Pnma) and $NaBH_4$ (cubic, S. G. F-43n). In addition, several unassigned peaks are visible. These peaks have been related to an unknown intermediate phase. In order to index the unassigned peaks, the PXRD pattern collected at the HZG was used. In fact, due to the rather low amount of the NaH phase, it appears more suitable for indexing than the one collected at UNITO. The experimental pattern collected at HZG (dots line at the figure top) and the calculated pattern from the contri-butions of the four known phases (continuous line at the figure top) are reported in Fig. 2. The result of subtracting the calculated pattern from the experimental one is also shown in the same figure (continuous line at the figure bottom). It gives the sequence of positions and relative intensities of diffrac-tion peaks of the unknown phase to be submitted to indexing step. However, the selection of peaks may be affected by the presence of glitches (see magnification of Fig. 2). This effect may occur especially close to the most intense peaks. Such

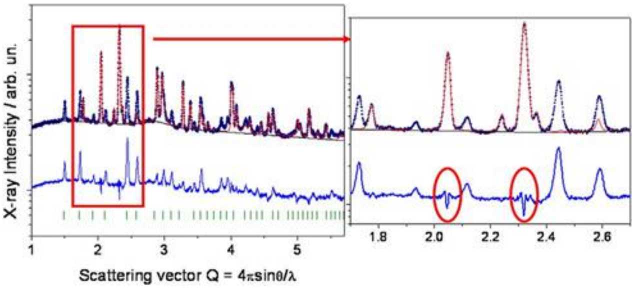

Fig. 2 e PXRD pattern collected at HZG (dots at the figure top) and calculated pattern from the contributions of the four known phases (continuous line at the figure top). The result of subtracting calculated from experimental pattern is shown as continuous line at the figure bottom. The series of hkl for the Pa-3 space group is reported as bars at the bottom of the figure. An enlargement is shown on the right hand side.

deviations of the plot difference with respect to a smooth trend can be attributed to inadequacies of the analytical pro-file functions to account precisely for the intensity distribu-tion of real diffraction peaks. In fact, bimodal or multimodal size distribution of crystallites and/or peculiar disorder model in the crystallites may represent physical circumstances for which simulated patterns are difficult to express adequately with a single-shape profile function [26].

The 2q values of 10 extracted peaks free from significant overlapping and considered to belong to the unknown phase, are reported in Table 1. The sequence of peak positions was least squares refined using the Maud-software [27] performing a Le Bail type approach [20] and corrected for the misalign-ment of the instrument as supplied by the fit to the other crystalline phases. To index the peaks belonging to the un-known compound, the McMaille [28] and Dicvol06 [29] pro-grams were employed. As a result, two possible cubic geometries P and I with lattice parameters of a ¼ 7.319(7) and 10.347(4) Å respectively were obtained. The results were also confirmed using the Maud program performing the Whole-Powder Pattern Indexing approach based on a Genetic Algo-rithm [30]. This method works differently from those used by the two programs, because it does not need any peaks list but it uses as indexing input only the experimentally collected pattern.

On the basis of the higher figure of merit (FoM) [31] ob-tained for the cell having lattice parameter equal to 7.319(7) Å, we decided to focus our attention on the cell with shorter lattice parameter. For the selected unary cells, the indexing sequence is reported in Table 1. For this unary cell, the FoM is rather high (roughly 100) and, in principle, either P23 or Pa-3 space groups are compatible with the systematic absences/ presences of experimental peaks, but after an analysis of the systematic absences the Pa-3 appears to be the most probable one. The series of hkl for the Pa-3 space group are reported at the bottom of Fig. 2.

In order to solve the structure from the indexed pattern, information about the chemical composition and density of the phase is necessary. Unfortunately, such data cannot be achieved experimentally, due to the presence of other compounds in the mixture. As far as the chemical composition is concerned, the experimental PXRD patterns have pointed out

Table 1 e List of ten hkl peaks that were indexed after analysis of the patterns of Fig. 1.

Peak no.	Observed 2q/	Observed intensity/arb. un.	hkl indices
1	21.000	72	(111)
2	24.320	99	(200)
3	27.230	24	(210)
4	29.900	36	(211)
5	34.650	170	(220)
6	36.820	100	(221)
7	42.800	50	(222)
8	44.630	20	(320)
9	49.840	10	(400)
10	56.240	23	(420)

Table 2 e Atomic coordinates of the boron-rich phase selecting the Pa-3 S.G. on the basis of a density of 2.197 g/cm^3 and 48 atoms in the unit cell.

Atomic coordinates and isotropic displacement parameters (in A$^{\circ 2}$)

Atom	Ox.	Wyck.	x/a	y/b	z/c	B
B1	þ0	24d	0.13816	0.45200	0.80463	4.5000
B2	þ0	24d	0.66727	0.04242	0.72033	4.5000

Crystal data

Formula sum	B_{48}
Formula weight	518.93
Crystal system	cubic
Space group	Pa-3 (no. 205)
Unit cell dimensions	a ¼ 7.3195(4) A$^{\circ}$
Cell volume	392.14(2) A$^{\circ 3}$
Density, calculated	2.197 g/cm^3
Pearson code	cP48
Formula type	N
Wyckoff sequence	d^2

the presence of both reactants and products of the reaction. As mentioned earlier, in the HZG sample, almost all NaH was reacted. During the hydrogenation of the 2NaH þ MgB_2 sys-tem, the unknown phase is observed to form just before the $NaMgH_3$ formation [15]. Therefore, boron being not present in $NaMgH_3$, we assume the occurrence of a boron-rich phase. In the absence of any experimental evaluation, we consider that this boron-based phase has density values similar to that of known boron allotropes. A list of calculated and measured densities for allotropes structures of boron (a,b,g and

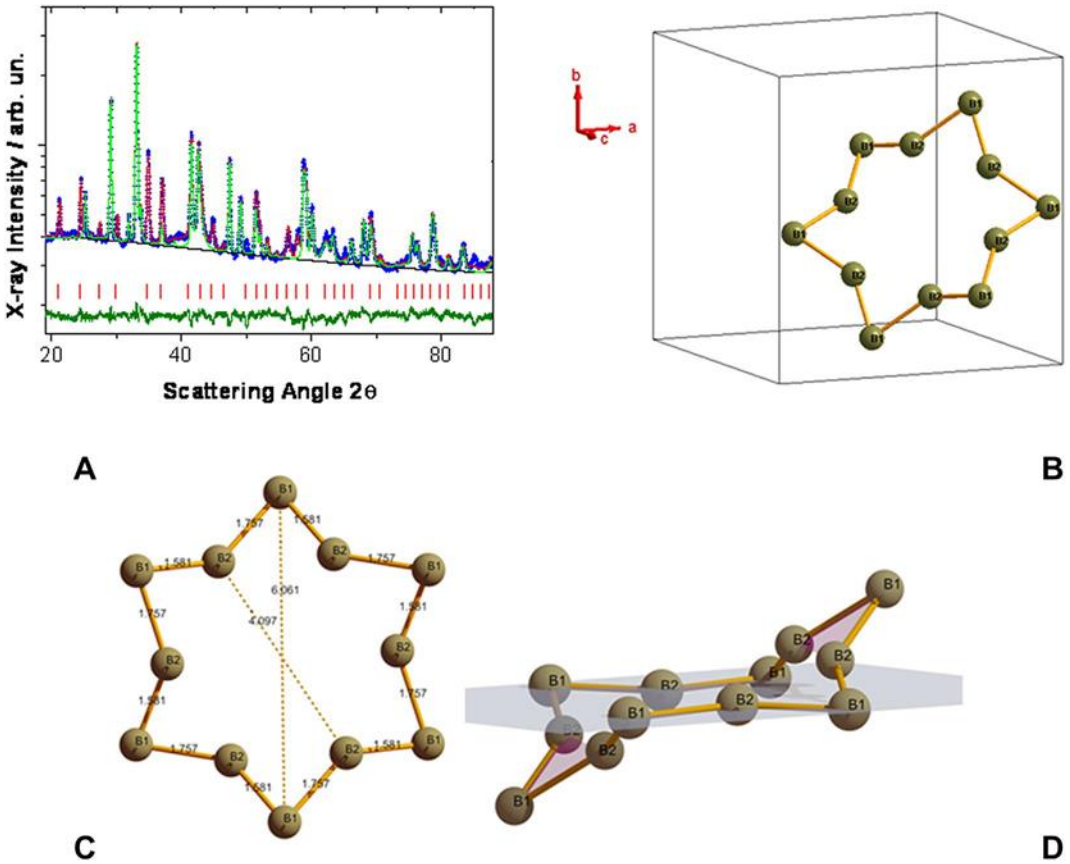

Fig. 3 e A: Rietveld fit to the total experimental pattern (dots) including the contribution of the proposed Pa-3 cubic (continuous line). Peak positions and residuals are shown in the bottom. B: Sketch of the B-atoms position in the unary cell, a cycle of twelve boron atoms. C: Alternating BeB bond length of 1.58 Å and 1.76 Å. D: Six of twelve atoms of the interconnected B-atoms lie on a plane.

tetragonal, respectively) has been reported in the literature [32e36], where values ranging from 2.20 to 2.52 g/cm^3 have been reported. The shortest BeB interatomic distance is 1.60 Å in the tetragonal structure, but similar values of 1.62 Å are reported also in the b-phase. The presence of anomalously shorter BeB distances may be a hint to evaluate the correct-ness of the obtained structure. Thus, the unit cell of cubic geometry with lattice parameter a ¼ 7.319 Å may contain reasonably from 48 to 52 boron atoms. Note also that some of the structures given for solving the b-boron allotrope entail an interatomic BeB distances below 1 Å, thus making doubtful some b-boron solutions as far as the fractional coordinates of atoms are concerned.

A parallel computation was performed using the list of hkl intensities and positions from Table 1 and the simulated annealing program Endeavour [37], reaching approximately the same result reported below. The boron fractional co-ordinates for this space group are reported in Table 2. This solution has the merit of showing BeB distances comprised in the range of values between 1.58 and 1.76 Å. These BeB dis-tance values are similar to those reported for the tetragonal boron (tP50). The overall Rietveld fit using the four known phases (i.e. NaH, MgB_2, $NaMgH_3$ and $NaBH_4$) plus the proposed cubic cP48 phase with space group Pa-3 is reported in Fig. 3A. A sketch of a possible connection scheme between alternating B_1 and B_2 Wyckoff sites shows the arrangement of two inter-connected hexagons, with BeB bond distance values of 1.581 and 1.757 Å, and angle value B2eB1eB2 of 75.562 as reported in Fig. 3B and C.

Six B-atoms lie on a plane and other six atoms are located above\under this plane, with B2-plane distances of 0.527 and 0.596 Å, and B1-plane distance of 1.421 Å (Fig. 3D).

The evaluation of such a description for the unknown phase using numerical indicators may not be entirely satis-factory because of the large number of phases present in the PXRD pattern. In particular, it is visible that some weak peaks are not taken into account in their intensity very accurately, thus suggesting to consider the possibility for a P23 space group. The adoption of this symmetry group leads to other proposals where the 48 atoms are located in 4 Wyckoff sites of j-type with multiplicity 12 (see Table 3). However, while adopting this space group, even if the Rietveld fit seems better, the presence of some BeB distances below 1.45 A˚ makes this solution less probable. It should be noted that other efforts to solve the structure with a larger unit cell of 10.347 A˚ and imposing cubic space group with inversion center I, ensuring the possibility to explore densities of 2.32 g/cm^3 were made. However, the given solutions failed again to give reliable interatomic BeB distances.

Table 3 e The Rietveld refined fractional coordinates obtained from Maud after selecting the P23 space group.

Atom	Wyck.	Site	x/a	y/b	z/c	˚ 2
B1	12j	1	0.72524	0.63871	0.96972	1.5
B2	12j	1	0.50001	0.70038	0.72399	1.5
B3	12j	1	0.75957	0.12208	0.42117	1.5
B4	12j	1	0.94935	0.27861	0.86913	1.5

The quantitative Rietveld's analysis of the diffraction pattern made considering the two possible space groups (Pa-3 and P23) shows an amount of the unknown phase considered constituted only by B-atoms, higher than 60 wt%. These values are higher than expected. In fact, considering a total conversion of the starting reactants into hydrogenated prod-ucts, the total amount of boron should be roughly 35 wt%. These results may be due to a reaction environment not totally controlled, allowing loss of reactants in the walls of the reactor.

Inclusion of other atoms like Mg and Na in the cubic lattice is possible in principle. Nevertheless, simulations in this sense suggested that other atoms inclusions must be kept low due to their different scattering factor. This is in agreement with a recent report on the MgeB phase diagram [38] where from semi-empirical thermodynamics calculations it was surmised that a B-rich phase may be privileged with approximate composition MgB_{20}. Of course, the presence of hydrogen atoms in the lattice cannot be rejected. Unfortunately their position in the unknown phase cannot be identified, because of negligible contributions to the X-ray diffraction patterns. The possibility to investigate the material by neutron scat-tering technique was considered, however, the absence of a proper boron isotope and the complexity of a possible neutron diffraction pattern containing multiple phases prevented us from applying this technique.

4. Conclusions

The structure of an unknown crystalline phase observed during the hydrogenation at high pressure of the system 2NaH þ MgB_2 was suggested. This phase can be envisaged by a cubic unit cell (a ¼ 7.3195(4) A˚, S. G. Pa-3) containing 48 boron atoms (cP48). In view of the estimated nearest neighbor BeB interatomic distances, the proposed structure gives a suitable approximation of the experimental pattern. More complex solutions, using bigger cells and more atoms (larger number of fractional coordinates), certainly describe more accurately the progression of relative intensities. However, those solutions fail to account properly for the interatomic BeB short distances.

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