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STUDIUL COMPUȘILOR INTERMETALICI TERNARI PE BAZĂ DE BOR ÎN SISTEMELE TERNARE *TR-MT-B* ($TR = La, Gd, Y; MT = Ni, Co, Fe$) A STUDY OF TERNARY INTERMETALLIC BORIDES IN THE *RE-TM-B* TERNARY SYSTEMS ($RE = La, Gd, Y; TM = Ni, Co, Fe$)

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The compounds synthesized in the ternary systems *La-TM-B*, *Gd-TM-B* et *Y-TM-B* ($TM = Ni, Fe, Co$) were studied in terms of their crystal structure, chemical composition and hydrogen sorption properties. Most of the compounds obtained in these systems crystallize with a $CeCo_4B$ type structure, with lattice parameters close to those of the compound $GdNi_4B$. A total replacement of Ni by Fe and/or Co is sometimes possible, meaning that a total solid solution exists between $RENi_4B$ and $REFe_4B$ or $RECo_4B$. Also, the boron is assumed to partially occupy two different crystallographic sites, although only one of these is mainly occupied by boron. The new phase $GdNi_{2.5}B_{2.5}$ was also observed in this study for the first time. In addition, a pseudo-binary phase GdB_3 is observed. Finally, it is reported that only the compound $LaNi_4B$ absorbs hydrogen, albeit irreversibly.

Compușii sintetizați în sistemele ternare *La-MT-B*, *Gd-MT-B* și *Y-MT-B* ($MT = Ni, Fe, Co$) au fost studiați din punct de vedere al structurii cristalografice, compoziției chimice și proprietăților de sorbție a hidrogenului. Majoritatea compușilor obținuți în aceste sisteme cristalizează cu o structură de tip $CeCo_4B$, având parametrii celulari apropiați de cei ai compusului $GdNi_4B$. Înlocuirea totală a Ni de către Fe și/sau Co poate avea loc uneori, semnificând existența unei soluții solide totale între $TRNi_4B$ și $TRFe_4B$ sau $TRCo_4B$. De asemenea, atomii de bor pot ocupa două poziții cristalografice diferite, una dintre acestea în proporție majoritară. În cadrul acestui studiu, o nouă fază de tip $GdNi_{2.5}B_{2.5}$ a fost identificată pentru prima dată. O fază pseudo-binară GdB_3 a fost de asemenea observată. În fine, absorbția de hidrogen are loc doar pentru compusul $LaNi_4B$, în mod ireversibil.

Keywords: intermetallics, borides, ternary compounds

1. Introduction

The introduction of hydrogen as an energy source, and the establishment of a "hydrogen economy" are conditioned by viable solutions for its production and storage. The hydrogen storage remains an important issue to resolve. At present, solid storage offers significant advantages in terms of safety and volumetric capacity. Nevertheless, if solid storage is promising in terms of safety and volumetric capacity, the weight capacity remains relatively low. Therefore, it is necessary to look for new materials and new compositions.

Among the binary intermetallics, Haucke phases of stoichiometry AB_5 , such as $LaNi_5$, present a great interest for hydrogen storage. Indeed, this compound reversibly absorbs 1.5 wt% hydrogen at room temperature [1]. We present in this work the study of $LaNi_5$ -derived substituted ternary compounds, by substitution of B for Ni, i.e. $RE(TM)_{5-x}B_x$ ($RE =$ rare earth, $TM =$ transition metal). Many ternary compounds can be derived from $LaNi_5$: these $RENi_{5-x}M_x$ compounds are

obtained by substitution of metal atoms for nickel on 3g sites ($M = Al, Fe, Co, Mn \dots$) or 2c sites ($M = Cu$) and for lanthanum on sites 1a ($RE = Y, Gd, Pr, \dots$). The main compounds synthesized in the ternary systems $RE(TM)_{5-x}B_x$ ($RE = La, Gd, Y, TM = Ni$) are of $RENi_4B$ type. A more or less systematic study is reported here on $RENi_{4-x}B_{1+x}$ and $RE(Fe/Co)_{4-x}B_x$ with $-0.5 < x < 0.5$ and $0 < y < 4$. It is also worth noting that boron was chosen for this study because some boron ternary compounds (e.g. $Nd_2Fe_{14}B$) exhibit original, remarkable magnetic properties; a comprehensive study of these properties is not discussed here but will be reported in the future.

2. Experimental details

All boron-based intermetallic compounds were synthesized from pure elements by melting in two steps: first fusion in an induction furnace, followed by a second one in an electric arc furnace. The fusion in an induction furnace does not melt the boron, due to its low electrical conductivity and

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its low thermal diffusion coefficient. The use of the electric arc furnace is necessary in order to ensure the fusion and diffusion of boron in the alloy.

This step was followed by heat treatment using variable durations and temperatures. Annealing allows in some cases to obtain improved crystallinity and purity of the samples. We have observed that the annealing conditions used in our study do not affect the composition and proportion of phases present.

Small blocks of materials thus obtained were pulverized using an agate mortar and pestle, and then characterized by X-ray powder diffraction; the data obtained was then used to perform a Rietveld refinement [2]. The background noise at low θ , visible on most diffraction patterns, is due to the sample holder in PMMA and the adhesive used to fix the powder on the sample holder.

X-ray diffraction analysis was performed using a Philips PANalytical X'Pert diffractometer, type PW1820 (ICMCB) or PW1050 (UPB) with Bragg-Brentano θ - θ geometry and Cu K α radiation ($\lambda_{K\alpha 1}=1.5405$ Å and $\lambda_{K\alpha 2}=1.5443$ Å). Data acquisition ($8^\circ < 2\theta < 80^\circ$) was performed with a 0.02° step and 30s constant counting time.

All samples synthesized in this study were also analyzed by electron microprobe, in order to determine their chemical composition. The samples were investigated by electron microprobe analysis using a CAMECA SX-100 instrument using pure metal samples as reference.

The hydrogen absorption and desorption tests were performed using an automated Sieverts-type gas titration apparatus C2-3000 (HERA® Hydrogen Systems) [3].

3. Results and discussion

3.1. Influence of rare earth on the structure

We first studied the influence of rare earth on the structure of three compounds of stoichiometry 1: 4: 1. The first compound in which we are interested is obtained from LaNi₅ by substitution of one B atom for a Ni atom. After melting and subsequent annealing at 800°C under vacuum for one week, the alloy obtained was analyzed by X-ray diffraction.

The Rietveld refinement of the diffraction pattern shows a single phase, as all the diffraction peaks were indexed on the basis of the La₃Ni₁₃B₂ structure type (with only few impurities present).

The Rietveld refinement parameters are summarized in Table 1. The lattice parameters and atomic positions estimated are in good agreement with the literature [4 - 7]. Initially, the refinement is carried out considering the B atoms replacing Ni on all sites. This refinement indicates that the initial rate of boron atoms present in sites 6i and 3g is zero. Thus, the substitution of boron for nickel preferentially takes place at sites 2c (82% occupied by B) and also 4h (17% occupied by B). A better refinement quality is obtained by considering that the boron atoms are substituted partially for nickel on crystallographic sites 4h, in addition to the boron located in 2c sites. Thus, the chemical formulation obtained is La₃Ni_{12.66}B_{2.34} or LaNi_{4.22}B_{0.78}. This composition remains close to the nominal composition.

The diffraction pattern also reveals the existence of impurities (LaNi₅ and La₂O₃). However, these impurities are present in quantities that are too small to be accurately quantified. There is a significant difference in lattice parameters: if the values of the *a* parameter differ slightly (*a* = 5.089 Å versus 5.016 for LaNi₅), the *c* parameter increases from 3.980 (8) Å (for LaNi₅) to 10.970 (3) Å in the case of La₃Ni₁₃B₂. This difference is given by the existence of a superlattice along the *c*-axis. The existence of single phase observed by X-ray diffraction analysis is confirmed by Castaing microprobe (Figure 1).

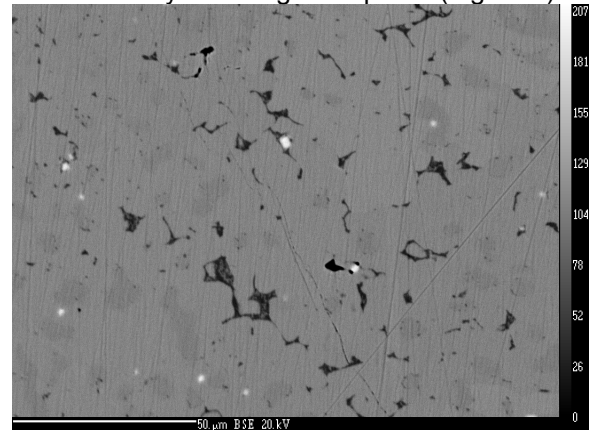


Fig. 1- Castaing microprobe of La₃Ni₁₃B₂ / Analiza prin microsonda Castaing a La₃Ni₁₃B₂.

Table 1

Rietveld refinement results for La₃Ni₁₃B₂ (S.G. P6/mmm) / Rezultatele rafinării Rietveld pentru La₃Ni₁₃B₂ (S.G. P6/mmm)

Lattice parameters Parametrii celulei	Atoms Atomi	Wyckoff position Pozitia Wyckoff	x	y	z	Occupation Ocuparea
<i>a</i> =5,089 Å	La1	1a	0	0	0	0.01466 (100%)
<i>c</i> =10,970 Å	La2	2 ^c	0	0	0.32289	0.08333 (100%)
Agreement factors Factori de calitate	Ni1	4h	1/3	2/3	0.32314	0.13796 (83%)
	B1	4h	1/3	2/3	0.32314	0.0287 (17%)
<i>R</i> _f =14,5%	Ni2	6i	1/2	0	0.85715	0.25 (100%)
<i>R</i> _{wp} =27,3%	Ni3	3g	1/2	0	1/2	0.125 (100%)
<i>R</i> _{Bragg} =11,6%	Ni4	2c	1/3	2/3	0	0.01436 (18%)
$\chi^2=4,3$	B4	2c	1/3	2/3	0	0.06897 (82%)

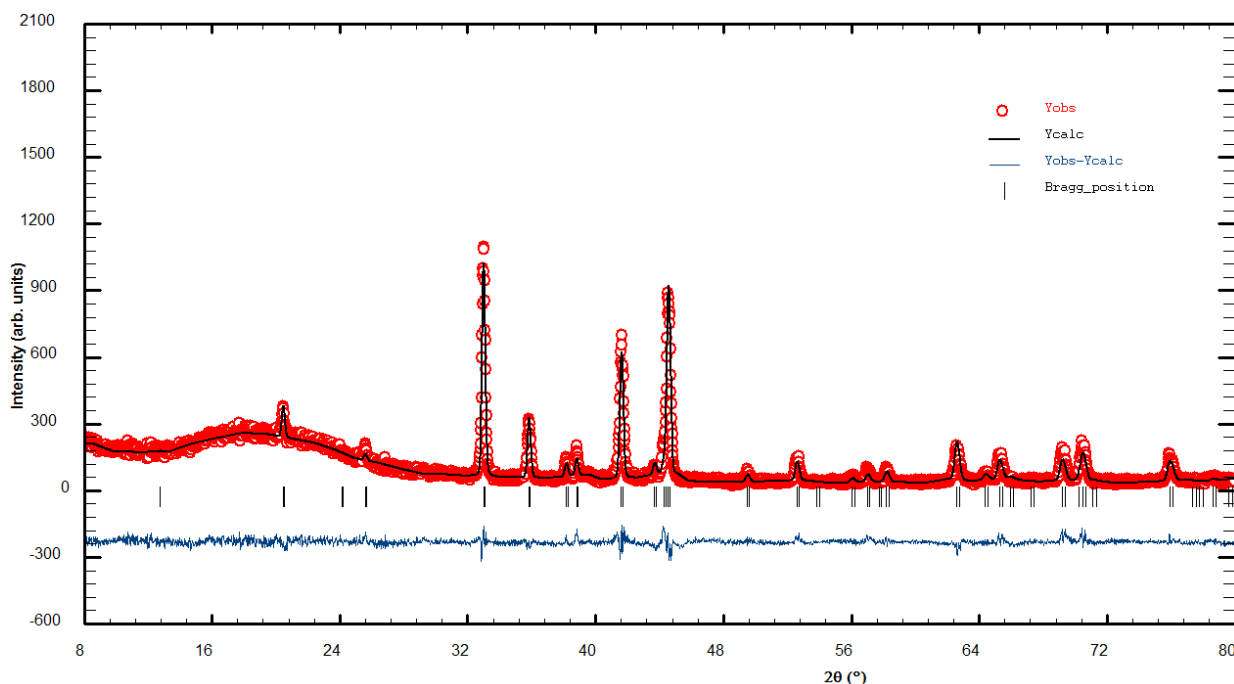


Fig. 2 - Rietveld refinement of X-ray diffraction pattern for GdNi₄B / Rafinarea Rietveld a difractogramei de raze X pentru GdNi₄B.

Table 1

Rietveld refinement results for GdNi₄B (S.G. P6/mmm) / Rezultatele rafinării Rietveld pentru GdNi₄B (S.G. P6/mmm)

Lattice parameters Parametrii celulei	Atoms Atomi	Wyckoff position Poziția Wyckoff	x	y	z	Occupation Ocuparea
a=5.009 Å						
c=6.956 Å	Gd1	1a	0	0	0	0.04166 (100%)
Agreement factors	Gd2	1b	0	0	1/2	0.04166 (100%)
Factori de calitate	Ni1	2c	1/3	2/3	0	0.07049 (85%)
R _i =13.2%	B1	2c	1/3	2/3	0	0.01284 (15%)
R _{wp} =31.4%	Ni2	6i	1/2	0	0.28840	0.25 (100%)
R _{Bragg} =14%	Ni3	2d	1/3	2/3	1/2	0.00802 (10%)
χ ² =1.4	B3	2d	1/3	2/3	1/2	0.07531 (90%)

The composition La₃Ni_{12.18}B_{2.88} is in good agreement with the phase La₃Ni_{12.66}B_{2.34} previously identified. Note however that the quantification of boron (Z = 5) by this method of analysis is far from precise. Most of the impurities observed (Figure 1) are identified qualitatively as oxides (e.g. La₂O₅) but the exact composition of the impurities is not precisely determined since they are present in insufficient quantity.

3.1.1. GdNi₄B

The X-ray diffraction of GdNi₄B (Figure 2) shows a single phase, with no observable impurities. The main refined parameters are given in Table 2.

It is worth noting that GdNi₄B crystallizes with the structure type CeCo₄B. In the plane perpendicular to the c axis (i.e. \vec{a}, \vec{b}), there are alternate planes TRNi₂ – Ni₃ – TRB₂ – Ni₃ – TRNi₂. Thus, the a parameter is retained, while the c parameter is almost double compared to LaNi₅.

Boron substitution for nickel takes place in sites 2c and 2d. However, most of the boron atoms are placed in 2d sites (90% boron) and only 15%

occupy 2c sites. The formulation obtained is GdNi_{3.95}B_{1.05}, very close to the nominal composition.

Electron microprobe analysis confirms the existence of a single phase with composition Gd_{1.01}Ni_{4.16}B_{0.83} (i.e., the total stoichiometry yields 6 atoms, equivalent to GdNi₄B), in good agreement with the nominal composition.



Fig. 3 - Electron microprobe analysis of GdNi₄B / Imagine de microscopie electronică pentru GdNi₄B.

Figure 3 represents the most oxidized area observed. However, the amount of oxide is generally very low, so that this phase is not detected by X-ray diffraction.

3.1.2. YNi_4B

The X-ray diffraction pattern obtained for the single-phase compound YNi_4B is in good agreement with the theoretical pattern. The structure identified by X-ray diffraction is in fact a superlattice, $Y_{0.915}Ni_{4.123}B$, already described by Belger et al.[8]. The lattice parameters of the superlattice are $a= 14.958 \text{ \AA}$ and $c= 6.946 \text{ \AA}$ (versus $a= 4.4977(4) \text{ \AA}$ and $c= 6.942(5) \text{ \AA}$ for YNi_4B), in good agreement with the literature. The results were confirmed by single crystal diffraction ($a= 14.9052 \text{ \AA}$ et $c= 6.9230 \text{ \AA}$).

3.2. $GdNi_{4-x}B_x$: Influence of boron content

We have varied the boron content in the compounds $GdNi_{4-x}B_x$ ($x= 0.5 ; 0.8 ; 1.2 ; 1.5$) to see if the under- or over-stoichiometry of boron can generate the formation of ternary phases with a stoichiometry different from 1: 4: 1. The data obtained show multiphase mixtures containing at least one phase in which the structure $GdNi_4B$ is maintained and other phases with an excess or a deficit of boron, as appropriate.

3.2.1. $GdNi_{4.5}B_{0.5}$

The Rietveld refinement of the X-ray diffractogram obtained was carried out using a mixture of two phases, a ternary composition close to $GdNi_4B$ and a binary composition, $GdNi_5$. The two phases are visible on the X-ray diffraction pattern and the percentages are 63% for $GdNi_4B$ and 37% for $GdNi_5$.

Considering $GdNi_{4.5}B_{0.5}$ is an equiatomic mixture of $GdNi_4B$ and $GdNi_5$, a 53 wt% percentage is obtained for $GdNi_5$. The result is in good agreement with that given by the Rietveld refinement of the X-ray diffraction pattern.

The lattice parameters for $GdNi_4B$ are similar to those previously calculated, indicating that the stoichiometry Ni / B must be identical. The decrease of the lattice parameters a and c actually leads to a decrease in the volume of only 1.64%.

Electron microprobe analysis (Figure 4) confirms these results and shows the two phases. Observed impurities (oxides) are present in small quantities. It is surprising to note the relatively regular distribution and homogeneity of the two phases.

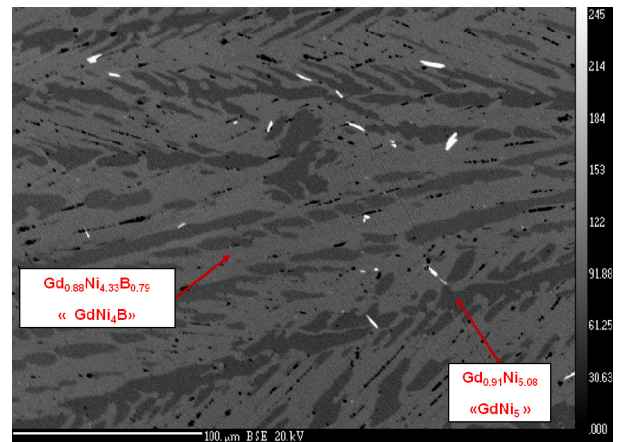


Fig.4 - Electron microprobe analysis of $GdNi_{4.5}B_{0.5}$
Imagine de microscopie electronică pentru $GdNi_{4.5}B_{0.5}$.

3.2.2. $GdNi_{4.2}B_{0.8}$

The X-ray diffraction pattern (Figure 5) shows double peaks, corresponding to two distinct

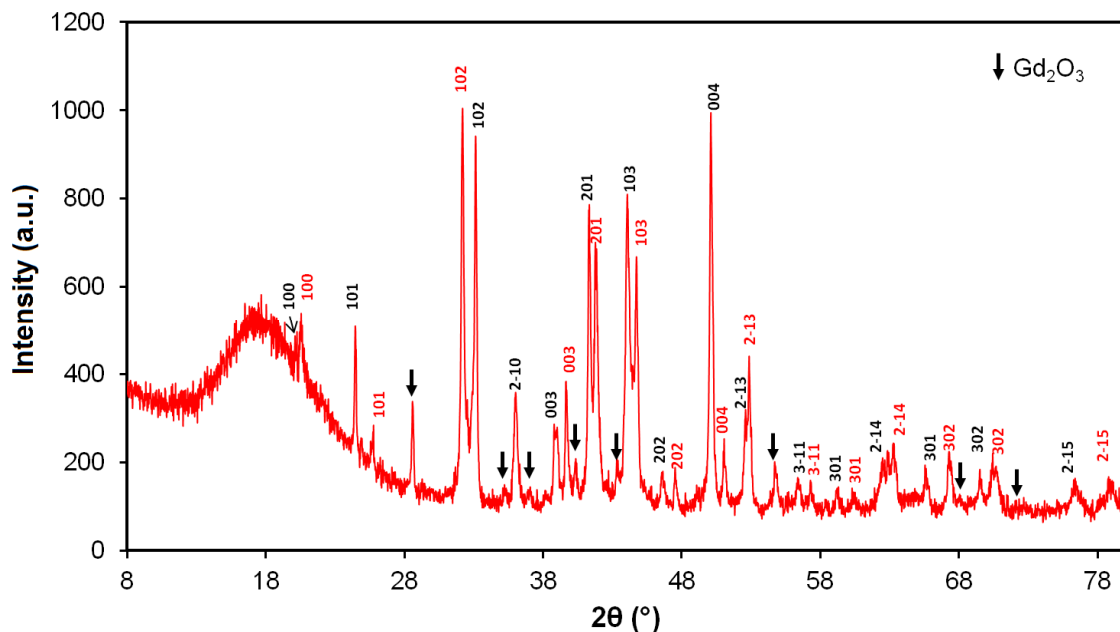


Fig. 5 - X-ray diffraction pattern for $GdNi_{4.2}B_{0.8}$, with indexed peaks corresponding to the two $GdNi_4B$ -type structures : $GdNi_{4.03}B_{0.59}$ / Diffractograma de raze X pentru $GdNi_{4.2}B_{0.8}$, cu picurile indexate corespunzând celor două structuri tip $GdNi_4B$: $GdNi_{4.2}B_{0.97}$ și $GdNi_{4.03}B_{0.59}$.

compounds with the $GdNi_4B$ structure and slightly different lattice parameters. For reasons unclear to this day, $GdNi_{4.2}B_{0.8}$ is the only composition synthesized in our study that displays this phenomenon.

Two kinds of annealing : 600°C for 2 months and 900°C for 10 days, led to similar results, indicating that there is no problem of thermodynamic stability. The two phases may correspond to the limits of the domain of existence for the phase $GdNi_4B$.

The lattice parameters of the two phases were determined by Le Bail refinement : $a = 4.956 \text{ \AA}$; $c = 6.914 \text{ \AA}$ and $a = 5.019 \text{ \AA}$; $c = 6.997 \text{ \AA}$. Note that this represents a volume change of only 3.6% for 12 atoms in the unit cell.

Microprobe analysis of this compound shows two different phases, with compositions approaching $GdNi_4B$: $GdNi_{4.2}B_{0.97}$ and $GdNi_{4.03}B_{0.59}$. Considering the atomic radii of Ni and B, we can reasonably assume that the phase richest in Ni is also the one with the greater lattice parameters.

3.2.3. $GdNi_{3.8}B_{1.2}$

The X-ray diffraction pattern, confirmed by microprobe analysis shows that the light boron over-stoichiometry leads to the formation of phase $GdNi_4B$.

The calculated lattice parameters are : $a = 4.973 \text{ \AA}$ and $c = 6.960 \text{ \AA}$ (i.e. $V = 149.06 \text{ \AA}^3$). These parameters are comparable to those obtained previously; it is not possible to conclude to any over- or under-stoichiometry of boron in the compound obtained.

The electron microprobe analysis reveals a $GdNi_{2.5}B_{2.5}$ type impurity. The excess boron

($GdNi_{4-x}B_{1+x}$) is thus concentrated in this low amount phase (not detected by X-ray diffraction). Thus, it is possible to conclude that the $GdNi_{3.8}B_{1.2}$ alloy consists in fact of a mixture of two phases : $GdNi_4B$ and $GdNi_{2.5}B_{2.5}$. The latter composition is reported here for the first time and is currently the subject of a more comprehensive study.

3.3. $GdNi_{4-x}TM_xB$ (TM=Fe, Co) : Substitution of other transition metals for Ni

Iron and cobalt are often used in materials for hydrogen storage (e.g. Co in $LaNi_5$ to improve the electrochemical cyclability and Fe in $TiNi$ to reduce the cost and improve performance [9, 10]).

3.3.1. $GdFe_4B$

The X-ray diffraction pattern (Figure 6) shows that the $CeCo_4B$ type structure is also retained for $GdFe_4B$ ($a = 5.089 \text{ \AA}$; $c = 6.822 \text{ \AA}$). The compound obtained is not pure; binaries $GdFe_2$, Fe_3B and Fe_2B are observed.

Variation of the annealing treatments: 2 months at 600°C and 10 days at 900°C) did not remove, nor at least limit the presence of binary phases in the compounds.

Analysis by electron microprobe confirms the X-ray diffraction results, although the Fe_2B phase is not detected by probe microanalysis.

3.3.2. $GdCo_4B$

The compound $GdCo_4B$, structure type $CeCo_4B$ ($a = 4.981 \text{ \AA}$; $c = 6.885 \text{ \AA}$) is synthesized with few impurities (Gd_2O_3). The lattice parameters are in good agreement with those found in the literature [11]. The composition is confirmed by electron microprobe analysis.

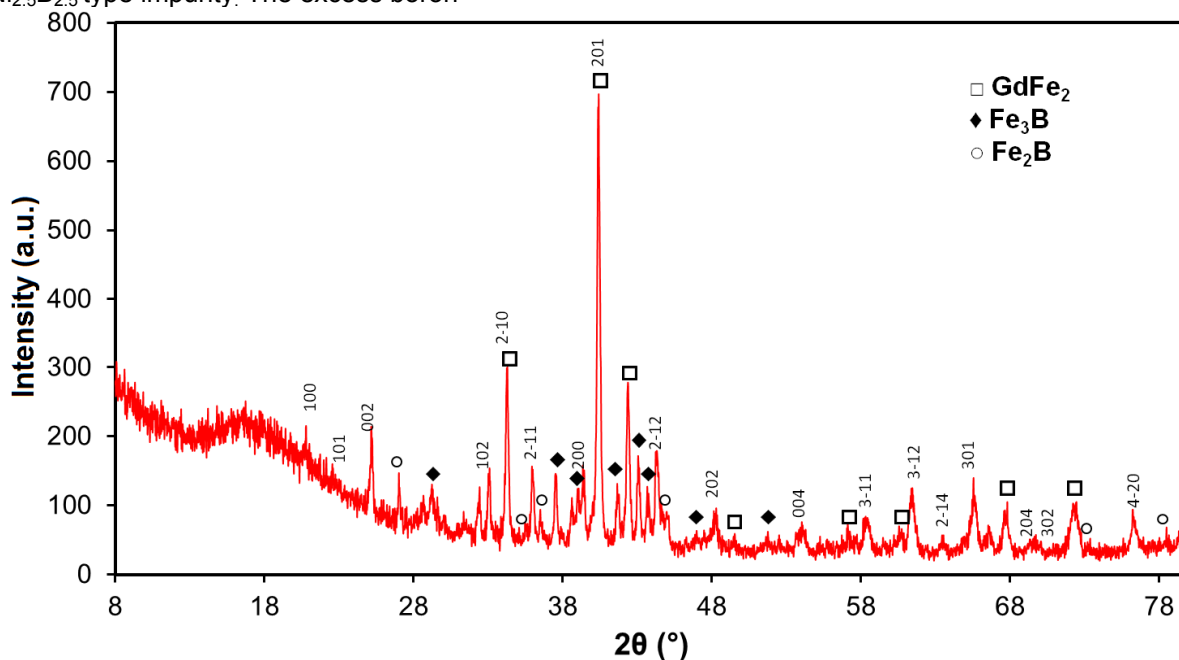


Fig. 6 - X-ray diffraction pattern for $GdFe_4B$, with indexed peaks for $GdFe_4B$ phase ($CeCo_4B$ type structure).
Difracograma de raze X pentru $GdFe_4B$, cu picurile indexate pentru faza $GdFe_4B$ (structura tip $CeCo_4B$).

Table 3

Rietveld refinement results for GdNi₂Co₂B (S.G. P6/mmm) / Rezultatele rafinării Rietveld pentru GdNi₂Co₂B (S.G. P6/mmm)

Lattice parameters Parametrii celulei	Atoms Atomi	Wyckoff position Poziția Wyckoff	x	y	z
a=5.031 Å c=6.929 Å					
Agreement factors Factori de calitate	Gd1	1a	0	0	0
R _f =24%	Gd2	1b	0	0	1/2
R _{wp} =36%	Co1/ Ni1	2c	1/3	2/3	0
R _{bragg} =22%	Ni2/ Co2	6i	1/2	0	0.28752
χ ² =2.7	B1	2d	1/3	2/3	1/2

3.3.3. GdNi₂Co₂B

As before, the X-ray diffraction allows us to identify a phase with structure type CeCo₄B ($a = 5.031 \text{ \AA}$; $c = 6.929 \text{ \AA}$). The Rietveld refinement results are shown in Table 3.

The composition GdNi₂Co₂B is confirmed by electron microprobe. The X-ray diffraction cannot make the difference between nickel and cobalt atoms, as their numbers of electrons are too close ($\Delta = 1$), and therefore the refinement does not provide information on the preferential localization of the two types of atoms. We therefore considered for the Rietveld refinement that the Co atoms replace Ni atoms in equal proportion (50%) on 2c and 6i sites. In addition, we have not considered the replacement of boron by a transition metal in 2d sites, in order to reduce the number of refined parameters.

However, studies in the literature state that the Ni atoms occupy 6i sites and Co atoms are located in 2c sites [12].

3.4. An overview of the synthesized RE(TM)_{4-x}B_x compounds

A summary of the main phases obtained after fusion and subsequent annealing is given in Table 2.

3.5. Hydrogenation properties

The hydrogen sorption properties (Figure 7) were studied using a hydriding PCT-03 (HERA Hydrogen Systems) automatic cycling apparatus. At room temperature and $P=10 \text{ bar H}_2$, absorption begins after approximately 7 minutes and reaches saturation after 17 minutes. The maximum absorption is 0.5 wt%, which corresponds to 1.92 H/ f.u. X-ray diffraction after absorption (Fig. 8) shows a shift of the peaks to the left (2θ decreases); the original structure is preserved, with an increase of the lattice parameters. As reported in Table 3, there is a strongly anisotropic variation of the lattice parameters. Indeed, the a

Table 2

An overview of the synthesized RE(TM)_{4-x}B_x compounds / Caracterizarea compușilor TR(TM)_{4-x}B_x

Composition Compoziție	Identified composition Compoziția determinată	Structure type Structura tip	Lattice parameters Parametrii celulei	Single phase Compus monofazic
LaNi ₄ B	La ₃ Ni _{12.66} B _{2.34}	La ₃ Ni ₁₃ B ₂	a=5.089 Å c=10.970 Å	Yes
GdNi ₄ B	GdNi _{3.95} B _{1.05}	CeCo ₄ B	a=5.009 Å c=6.956 Å	Yes
YNi ₄ B	Y _{1.1} Ni _{4.33} B	Y _{0.915} Ni _{4.123} B	a= 14.958 Å c= 6.946 Å	Yes
GdNi _{4.5} B _{0.5}	GdNi ₄ B GdNi ₅	CeCo ₄ B CaCu ₅	a=4.978 Å c=6.927 Å a=4.915 Å c=3.962 Å	No
GdNi _{4.2} B _{0.8}	GdNi _{4.2} B _{0.97} GdNi _{4.03} B _{0.59}	CeCo ₄ B CeCo ₄ B	a = 5.019 Å c = 6.997 Å a = 4.956 Å c = 6.914 Å	No
GdNi _{3.8} B _{1.2}	GdNi _{3.78} B _{1.06}	CeCo ₄ B	a = 4.973 Å c = 6.960 Å	No (Impurities = GdNi _{2.5} B _{2.5})
GdNi _{3.5} B _{1.5}	GdNi _{4.33} B _{1.12} GdNi _{2.5} B _{2.5}	CeCo ₄ B ?	a = 4.992 Å c = 6.906 Å -	No
GdFe ₄ B	GdFe ₄ B	CeCo ₄ B	a = 5.089 Å c = 6.822 Å	No (Impurities= GdFe ₂ , Fe ₃ B, Fe ₂ B)
GdCo ₄ B	GdCo _{4.26} B _{0.88}	CeCo ₄ B	a = 4.981 Å c = 6.885 Å	Yes
GdNi ₂ Co ₂ B	GdNi _{2.05} Co _{2.06} B _{1.07}	CeCo ₄ B	a=5.031 Å c=6.929 Å	Yes

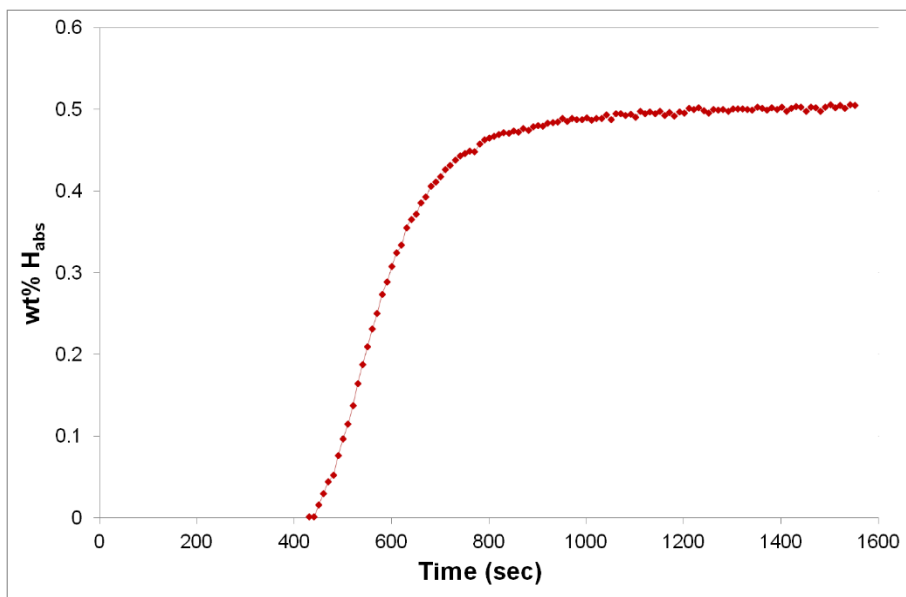


Fig. 7 - Absorption kinetics for LaNi₄B at T=25°C and P=10bar H₂ / Cinetica de absorbție pentru LaNi₄B la T=25°C și P=10bar H₂.

Table 3

Lattice parameters for LaNi_{4,33}B_{0,67} before and after hydrogenation
 Parametrii celulei elementare pentru compusul LaNi_{4,33}B_{0,67}, înainte și după hidrogenare

	a (Å)	c (Å)	Δa (%)	Δc (%)	ΔV (%)
LaNi ₄ B	5.092	10.980	-	-	-
LaNi ₄ BH _{1,92}	5.289	11.100	3.87	1.09	9.07

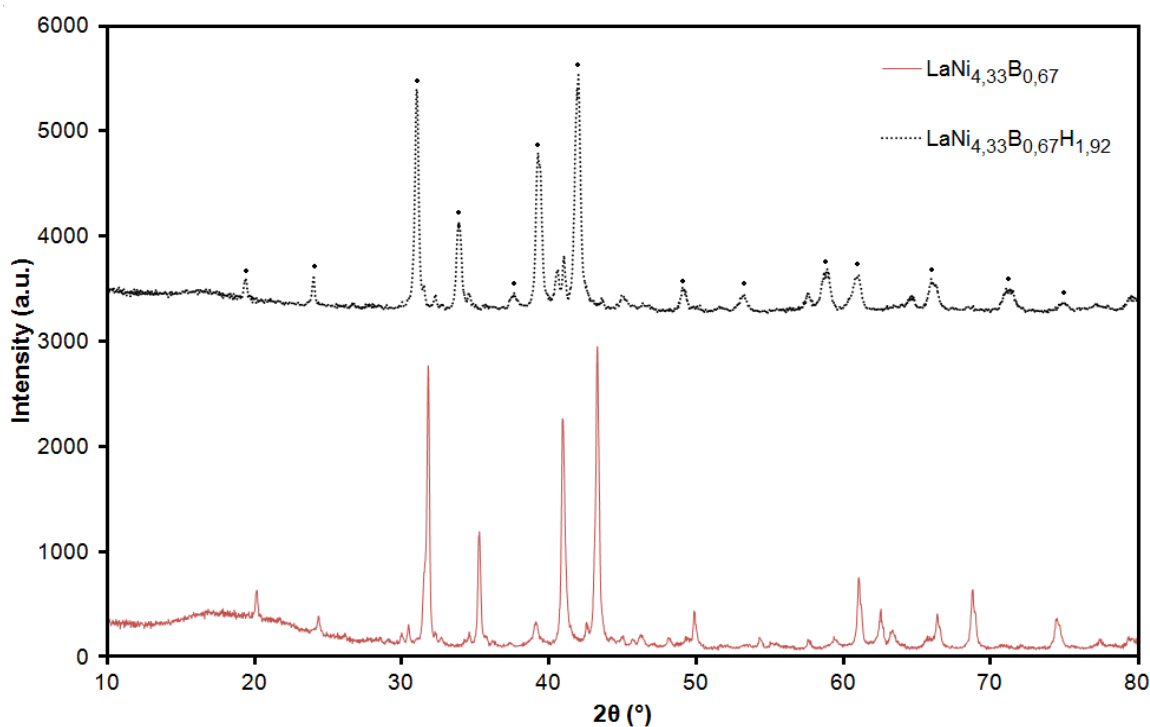


Fig. 8- X-ray diffraction patterns for LaNi₄B after annealing (1 week at 900°C) and hydruation : there is a shift of the peaks to the left, indicating the expansion of the lattice; the structure is retained. Almost all of the peaks are indexed with structure LaNi₄B₀. Difractogramele de raze X pentru compusul LaNi₄B după tratamentul termic (1 săptămână la 900°C) și respectiv hidrogenare: se observă un decalaj al picurilor spre stanga, corespunzător creșterii volumului celulei, cu conservarea parametrilor. Picurile sunt în majoritate indexate cu structura tip LaNi₄B.

parameter has increased by nearly 4%, while the c parameter increases by only 1% after hydrogenation. This leads to a volume change of 9.07%, in good agreement with the number of hydrogen atoms absorbed by the compound (2-4%

increase in volume per hydrogen atom). There is no observed desorption under dynamic vacuum at 50°, 100° and 300°C. The hydrided compound is particularly stable.

The hydrogenation does not have the same effect on the substituted boron compounds as on LaNi₅ [13,14]. Indeed, in the case of LaNi₅, the weight percentage of absorbed hydrogen is 1.5% and the absorption is reversible under moderate conditions (20°C ; 3.4 bar).

We wish to clarify that the compound LaNi₄B has already been studied in literature [4,15]. We have synthesized this compound for use as a standard for the different boron-substituted compounds analyzed in our study. However, we were not able to reproduce the results previously obtained for this compound, namely the reversible sorption at room temperature [4]; our results are therefore in contradiction with the results in the literature.

For all other compounds previously studied, no hydrogen absorption could be measured. It can be noted that some similar compositions, previously studied in the literature, have exhibited sorption properties. Again, our results are in contradiction with the results in the literature. Note that we have varied the activation conditions (up to 300°C under primary dynamic vacuum) and absorption conditions (up to 50 bar hydrogen pressure and 300°C) with no success.

4. Conclusions

The compounds synthesized in the ternary systems La-TM-B, Gd-TM-B and Y-TM-B (TM=Ni, Fe, Co) were studied in terms of their crystal structure, chemical composition and hydrogen sorption properties.

We found that most of the compounds obtained in these systems crystallize with a CeCo₄B type structure, with lattice parameters close to those of the compound GdNi₄B. Most of the results are summarized in Table 2. Notable exceptions are the compositions LaNi₄B (de La₃Ni₁₃B₂ type structure) and YNi₄B (Y_{0.915}Ni_{4.123}B-type superlattice).

We also found that a total solid solution exist between GdNi₄B and GdCo₄B. With Fe, a solid solution also exists but it has not been possible to obtain a single phase ternary compound (impurities such as Fe₂B, GdFe₂ are observed).

Varying the boron content in GdNi₄B leads to the obtention of a new ternary phase of composition close to GdNi_{2.5}B_{2.5} but with a structure that is not defined at the moment.

Finally, all the compounds studied share a common trait, in that they do not absorb hydrogen even under severe conditions (i.e., up to 500°C and 60bar H₂), with the exception of LaNi₄B. In this case, an irreversible sorption of 2 hydrogen atoms/f.u. is reported.

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