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Rich magnesium ternary compound so-called $LaCuMg_8$ derived from La_2Mg_{17}. Structure and hydrogenation behavior

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ABSTRACT

The magnesium metal rich composition $La_{10}TM_{10}Mg_{80}$ (with TM = Ni and Cu) were synthesized from the elements in sealed tantalum tubes in an induction furnace. The results show differences depending on the transition metal used. The sample with Ni demixed into ternary and binary compounds with composition close to $LaMgNi_2$, La_2Mg_{17} and Mg_2Ni. Only the sample with copper forms a ternary compound. Crystal structure of this new compound was determined by X-ray diffraction on single crystals with an exact formulation $La_{1.744(5)}Cu_{1.53(5)}Mg_{15.73(4)}$. It crystallizes with the La_2Mg_{17} structure type, space group $P6_3/mmc$, $a = 10.1254(2)$ Å and $c = 10.0751(2)$ Å. The Mg atoms form hexagonal tubes along the *c*-axis filled by La and Mg. The Cu atoms are located in these tubes on or around the La and Mg positions, inducing disorder. This compound so-called $LaCuMg_8$ absorbs around 2 wt% of hydrogen at 603 K, 30 bar and reversibility is possible. Nevertheless, after the first hydrogenation, decomposition into MgH_2, LaH_3 and $MgCu_2$ have been shown. The pathway of the reaction is described herein.

1. Introduction

The rare earth (RE) – transition metal (T) – magnesium systems have been intensively investigated in recent years [1]. It was shown that these systems are interesting from various points of view: structural, magnetic and hydrogenation behavior. For example, RE_4NiMg (with RE = Y, Pr–Nd, Sm, Gd–Tm, Lu) crystallizing in cubic structure with Mg_4 tetrahedra, absorbs up to 11 hydrogen atoms per formula unit [2].

The Mg rich systems are still not well known. It is therefore established that some compounds containing a high Mg content exhibit interesting mechanical [3] or hydrogenation properties [4]. Indeed, Mg presents a high-strength, a low cost, a really low weight and a strong chemical affinity with hydrogen.

In order to highlight new systems, the ternary diagrams La–TM–Mg in the Mg rich region have been investigated (with TM = Cu and Ni). Some other researches have already shown the existence of new ternary compounds in the system Y–Cu–Mg, La–Cu–Mg and Tb–Cu–Mg for example [5–7]. The new compound so-called $LaCuMg_8$ was brought to light but the same composition with Ni leads to a demixion into known ternary and binary compounds in agreement with previous studies on La_2Mg_{17}–Ni composites [8]. In this paper, we report on its crystallographic properties and hydrogenation behavior. The structural modifications induced by Cu insertion are discussed.

2. Experimental

2.1. Syntheses and characterization

Starting materials for the preparation of the samples $La_{10}Cu_{10}Mg_{80}$ and $La_{10}Ni_{10}Mg_{80}$ were a lanthanum pieces (Stream Chemicals, >99.9%), a nickel rod (Stream Chemicals, >99.9%), a copper rod (Good fellow, >99.9%) and a magnesium rod (alpha Aesar, >99.8%). To avoid oxides impurities, the surfaces of the magnesium and lanthanum pieces were carefully removed on a turning lathe. Elemental pieces were then weighted in the appropriate amounts and sealed in small tantalum ampoules under an argon pressure of ca. 800 mbar. The argon was purified before with magnesium sponge (873 K). Then, the ampoules were placed in a high frequency furnace under argon and heated at about 1373 K and kept at that temperature for 2 min. The ampoules were then annealed under vacuum at 673 K for two weeks. Finally the tubes were quenched to room temperature. No reaction with the tantalum tubes was observed. The polycrystalline samples are stable in air.

The bulk samples were investigated by electron probe micro-analyses (EPMA) with La, Ni, Cu, and Mg, as standards. The bulk samples were embedded in a methylmetacrylate matrix and the

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surface was polished with different silica and diamond pastes. The surface remained unetched for the EPMA measurements.

All polycrystalline samples were characterized with X-ray powder diffraction using a Philips PW 1050 diffractometer with CuKα radiation ($\lambda = 0.15405$ nm). These patterns were scanned by steps of 0.02° (2θ) from 5° to 80° with a constant counting time of 30 s they were analyzed by full patterns matching using the FULLPROF program [9].

2.2. Structural determination

A crystal suitable for single-crystal X-ray diffraction was selected on the basis of the size and sharpness of the diffraction spots. Data collection was carried out on an Enraf-Nonius Kappa CCD diffractometer using Mo Kα radiation. Data processing and all of the refinements were performed with the Jana2006 program package [10]. A Gaussian-type absorption correction was applied, and the shape was determined with the video microscope of the Kappa CCD. Details of data collections and structure refinements are listed in Table 1.

The extinction conditions observed agree with the $P6_3/mmc$ space group. To start the refinement the atomic coordinates of La_2Mg_{17} were introduced [11]. After few cycles very high values of the reliability factors were observed with negative isotropic Atomic Displacement Parameters (ADPs) for all positions. From Fourier-difference and Fourier maps analysis it appeared clearly that the La1 position was splitted and non-fully occupied. Moreover small peaks in the (0 0 z) and (1/3 2/3 z) chains were observed. The copper positions Cu1a and Cu1b were introduced in the (0 0 z) chain and the Cu2 position in the chain (1/3 2/3 z). The attribution of these electron residues to copper atoms was based on the analysis of the ADP parameters and the stoichiometry deduced from microprobe analysis. Negative residues on the Fourier-difference map on the Mg2 position were removed by a mixing of copper and magnesium. To avoid strong correlations in the refinement the ADP parameters were constrained to the same values for Cu1a and Cu1b and for Cu2 and Mg2. The occupancy factors of La1, Cu1a and Cu1b were constrained to correspond to a fully-occupied La1 position. The chemical formula deduced from the occupancy factors refinement led to the overall composition $La_{1.744(5)}Cu_{1.53(5)}Mg_{15.73(4)}$. The refined atomic positions and equivalent atomic displacement parameters are given in Table 2. Further details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-421758.

Table 1
Crystal data and structure refinement[a] for the so-called $LaCuMg_8$ compound.

Chemical formula from X-ray diffraction	$La_{1.744(5)}Cu_{1.53(5)}Mg_{15.73(4)}$
Chemical formula from EPMA	$La_2Cu_{1.71}Mg_{15.295}$
Cell setting, space group	Hexagonal, $P6_3/mmc$
a, c (Å)	10.158(2), 10.059(2)
Z, D_x (Mg m^{-3})	2, 2.666
Radiation type, μ (mm^{-1})	Mo $K\alpha$, 6.47
Diffractometer	Nonius Kappa CCD
Absorption correction, shape	Gaussian, block
T_{min}, T_{max}	0.710, 0.782
No. of measured, independent reflections, R_{int}	10 295, 440, 0.079
No. of observed reflections ($I > 2\sigma(I)$)	327
$2\theta_{max}$ (°)	56.0
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.088, 1.58
No. of reflections, of refined parameters	440, 35
Weighting scheme	$w = 1/(\sigma^2(I) + 0.0009I^2)$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.68, −0.86

[a] Computer programs: Jana2006 [10].

Table 2
Atomic positions and equivalent displacement parameters of $La_{1.744(5)}Cu_{1.53(5)}Mg_{15.73(4)}$, so-called $LaCuMg_8$.

Position	Wyck.	Occ	x	y	z	U_{eq} (Å^2)
La1	4*e*	0.372(2)	0	0	0.2196(2)	0.0186(7)
Cu1a	4*e*	0.081(3)	0	0	0.098(2)	0.026(4)
Cu1b	2*a*	0.093	0	0	0	0.026
La2	2*d*	1	1/3	2/3	3/4	0.0157(3)
Mg1	4*f*	0.911(7)	1/3	2/3	0.1000(4)	0.0219(12)
Cu1	4*f*	0.089	1/3	2/3	0.2156(15)	0.027(7)
Mg2	6*g*	0.634(7)	1/2	0	0	0.0218(9)
Cu2	6*g*	0.366	1/2	0	0	0.0218
Mg3	12*j*	1	0.3319(3)	0.9676(3)	1/4	0.0330(11)
Mg4	12*k*	1	0.1687(2)	0.3375(3)	0.9816(2)	0.0233(9)

2.3. Hydrogen sorption

Hydrogen sorption kinetics were investigated by use of an automatic Sievert-type volumetric apparatus (HERA, Hydrogen Storage System) in the temperature range from room temperature to 623 K and with 30 bar of H_2.

3. Results and discussion

3.1. Syntheses

The X-ray powder patterns of $La_{10}Cu_{10}Mg_{80}$ and $La_{10}Ni_{10}Mg_{80}$ samples after heat treatment are shown in Fig. 1. Drastic differences can be observed between both samples. The $La_{10}Ni_{10}Mg_{80}$ pattern is indexed with different known phases (i.e. La_2Mg_{17}, $LaNiMg_2$, $LaMg_3$, Mg_2Ni). For $La_{10}Cu_{10}Mg_{80}$, only the structure La_2Mg_{17} is identified with a low shift toward the higher 2θ angles indicating smaller cell parameters. The EPMA on both samples (Fig. 2 for $La_{10}Ni_{10}Mg_{80}$ and Fig. 3 for $La_{10}Cu_{10}Mg_{80}$), confirms the previous X-ray powder analyses. Fig. 2 shows four phases (e.g. $La_{9.9}Ni_{3.1}Mg_{87}$, $La_{22.8}Ni_{25.6}Mg_{51.6}$, Mg_2Ni and $LaMg_3$) close to the composition identified by X-ray powder for $La_{10}Ni_{10}Mg_{80}$. The amount of Ni in the composition determined by EPMA should be considered as slightly overestimated as the $La_{22.8}Ni_{25.6}Mg_{51.6}$ corresponds to the $LaNiMg_2$ compound. Therefore the composition of the main phase should be considered as La_2Mg_{17} with a very small contain of Ni. This is confirmed by the cell parameters determined by X-ray

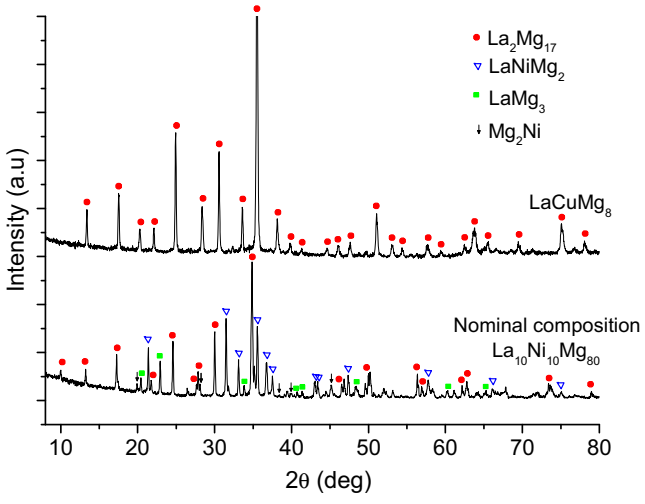

Fig. 1. XRD pattern of sample with nominal composition $La_{10}Ni_{10}Mg_{80}$ (down) and $La_{10}Cu_{10}Mg_{80}$ (up).