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A reactivity study in the Mg–B system reaching for an improved synthesis of pure MgB₂

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Abstract

The binary Mg–B system was studied with respect to the existing phases MgB₂, MgB₄, MgB₇, and MgB₁₂ and their transformations into each other. As a result of these studies, a new synthesis route is reported for MgB₂ by reacting MgB₄ and Mg with each other. The obtained MgB₂ was characterized by Rietveld refinement of the powder XRD pattern ($R_{Bragg} = 3.56\%$, $R_{wp} = 10.6\%$), magnetic measurements, and by electron probe microanalysis (EPMA). With this new synthesis route, a better phase homogeneity is obtained when compared with MgB₂ samples prepared from the elements.

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1. Introduction

The recent discovery of superconductivity in MgB₂, a compound known for decades, with the remarkably high transition temperature of 39 K [1] has attracted great interest, because it introduces a new, simple binary superconductor with record high superconducting transition temperature for a non-oxide and non-C₆₀-based compound. MgB₂ appears to have many advantages in application compared to Nb₃Ge, which are on the one hand the nearly twice as high transition temperature and on the other the clearly lower weight. For this reason, there were made numerous attempts concerning the synthesis of MgB₂ [2-5], and theoretical calculations [6-8]. Variations in the chemical composition of MgB_2 [9], like the doping with carbon in the boron network [10,11] or the Al substitution [12-14], did not lead to an improvement of the superconducting properties. Carbon doping by CVD process leads to an increase of $H_{c2}(0)$ from 16 to 32 T but to a lower of the transition temperature of 36.2 K [15].

The synthesis of the *ordinary* compound MgB₂ has turned out to be more difficult than expected, especially when a high yield of a high-purity sample is desired. These difficulties are related to the chemical and thermodynamic features of the Mg–B system. If the elements boron and magnesium are used for preparation, a higher Mg-boride, MgB₁₂, is always formed [16]. Once MgB₂ is annealed at temperatures higher than the melting temperature of magnesium (650 °C), which is inevitable in the synthesis process, the material turns to become more and more Mg deficient. In addition, traces of MgO are discovered as the most common impurity in nearly all preparations. For this reason, new reaction channels must be found to improve the methods of synthesis for MgB₂, and on this basis to allow a specific introduction of pinning centres.

The phase diagram for the Mg–B system is not yet completely available. At present five phases, MgB₂, MgB₄, MgB₇, MgB₁₂, and MgB₂₀, were reported in this binary system. The characterisation of MgB₂ was first published by Jones and March [17] in 1953. MgB₂ crystallizes in the

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hexagonal AlB₂ type in the space group *P6/mmm* with the lattice parameters a = 3.0834(3) Å, c = 3.522(2) Å. The crystal structure of MgB₄ was refined by Naslain et al. [18] in the orthorhombic space group *Pnam* with the lattice parameters a = 5.464(3) Å, b = 7.472(3) Å, and c = 4.428(3) Å. Guette et al. [19] reported the determination of the crystal structure of MgB₇, which crystallizes in the space group *Imam* with a = 5.597(3) Å, b = 8.125(3) Å, and c = 10.480(5) Å. The compositions MgB₁₂ and MgB₂₀ can be considered as stuffed derivatives of the structure of β -rhombohedral boron ($R\bar{3}m$, a = 10.932(2) Å, c = 23.819(5) Å [20]). MgB₁₂[21,16] and MgB₂₀[22] also crystallize rhombohedral with their lattice parameters of a = 11.014(7) Å, c = 24.170(2) Å and a = 10.9830(4) Å, c = 24.1561(2) Å being closely related to those of β -rhombohedral boron.

In this paper, we report a new synthesis route for MgB_2 and we present a possible reaction scheme that correlates the different Mg-B phases MgB_2 , MgB_4 , MgB_7 , and MgB_{12} and supplements the calculated binary Mg-B phase diagram [23].

2. Experimental

2.1. Syntheses

All manipulations for the synthesis of the magnesium borides were performed in an Ar filled glove-box (MBraun) with magnesium (chips 99+, Strem) and β -rhombohedral boron (crystal powder 99.7%, ABCR) as starting materials. Appropriate quantities of Mg and B were filled into niobium containers, which were sealed under Ar with an electric arc and then placed into a vacuum-sealed silica ampoule. Four types of samples are referenced here (1–4) with respect to their syntheses and compositions, as examined by means of powder XRD and EPMA.

 MgB_{12} (sample 1) was synthesized from stoichiometric (1:12) quantities of Mg and B, heated at 1000 °C for 3 weeks.

MgB₄ (sample 2) was synthesized from stoichiometric (1:4) quantities of Mg and B. The sample was first heated to 650 °C for one day and then heated to 1200 °C and remained at this temperature for 5 days.

A typical sample of MgB₂ (sample 3) was prepared by the common way from the elements with the nominal composition Mg:B = 1:3 at 850 °C for 3 days. To our experience, this composition leads to higher yields of MgB₂ (90%) than the 1:2 composition (70%). Reaction products contained MgB₂ besides MgB₁₂ and unreacted magnesium. The remained metal can be edulcorated with a solution of EtOH/I₂ from the reaction product.

In a different set of reactions MgB_2 (sample 4) was synthesized from MgB_4 . For this reaction the previously prepared MgB_4 was sealed with an equal molar quantity of magnesium into a niobium container, fused into an evacuated silica tube, and heated at 750 °C for 5 days. After cooling down slowly, a grey micro-crystalline powder of MgB_2 (sample 4) was obtained as the only product detectable in the X-ray powder pattern.

2.2. X-ray diffraction studies

The reaction products were inspected with an X-ray powder transmission diffractometer (STOE, StadIP) using monochromatic Cu- $K_{\alpha l}$ radiation. The XRD pattern of samples 1–4 were indexed in accord with the literature data. Samples were obtained X-ray pure. Only the powder pattern of sample 3 showed some MgB₁₂ as a side phase. An additional XRD powder pattern was recorded for MgB₂ (sample 4) in a reflection set-up with a Philips PW 1830 diffractometer. This powder pattern was indexed and the crystal structure was refined with the aid of the program FullProf [24] (Fig. 1). Results of the structure refinement are given in Table 1. Atom positions and isotropic displacement parameters are provided in Table 2. The refined pattern is shown in Fig. 1.



Fig. 1. Observed (solid line) and calculated (discrete points) XRD-powder pattern of MgB₂ (sample 4) with Bragg reflections, and the difference curve.

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Table 1 Crystal data and parameters for data collection and structure refinement of MgB₂

** *******	
Sum formula	MgB ₂
Formula weight	45.927 g/mol
Temperature	298 K
Wave length	154.051 pm CuK _{α1} , 154.433 pm CuK _{α2}
Crystal system	Hexagonal
Space group	P61mmm
Lattice parameters	a = b = 308.468(8) pm, c = 352.44(1) pm
Measured range	$20^\circ \leqslant 2\theta \leqslant 130^\circ$
Independent reflections	22
Refined parameters	19
R _{Bragg}	3.56%
R _{wp}	10.6%
R _p	9.59%
χ^2	3.61

Table 2	
Atomic coordinates and isotropic displacement parameters	

Atom	Wyckoff- Position	x/a	y/b	z/c	$U_{\rm eq}/{ m \AA}^2$	Occupation
Mg	1a	0	0	0	0.0197(3)	0.9360(1)
В	2d	1/3	2/3	1/2	0.0254(6)	1

The correlation between U_{eq} and the occupation of Mg is 0.08.

2.3. Magnetic studies

The magnetic susceptibility of MgB₂ (sample 4) was studied with a SQUID magnetometer (Quantum Design, MPMS) in the temperature region between 5 and 50 K using a static field (H = 20 G). A sample of MgB₂ was used for the measurement in a gelatine capsule. The compound showed superconducting behavior with a transition temperature of 39 K (Fig. 2).

2.4. EPMA analysis

The samples for EPMA examinations were prepared as reported in [16]. EPMA-WDX analyses were performed with a JEOL 8900 RL Superprobe operated at 15 kV acceleration voltage and a probe current of 15 nA. The electron beam was generally focused (<1 μ m diameter). LDEB, TAP and LDE1H crystals were used as analyzing crystals for B, Mg, and O K_{α} X-rays, respectively. Synthetic MgO and metallic β -B (99.994 wt.% B) were used as standards for the calibration. Whereas Mg and O were

Table 3 Results of WDX analysis of powder samples 1–4

Sample	B in wt.%	Mg in wt.%	O in wt.%	Totals in wt.%	Composition
1 (MgB ₁₂)	84.89	15.81	0^{a}	100.7	MgB _{12.07}
	85.14	14.46	0^{a}	99.6	MgB _{13.24}
	84.64	14.95	0.05	99.64	MgB _{12.73}
	84.41	15.65	0^{a}	99.86	MgB _{12.13}
	83.7	16.15	0^{a}	99.86	MgB _{11.65}
2 (MgB ₄)	65.34	34.28	0.74	100.36	MgB _{4.29}
	64.23	34.49	1.05	99.77	MgB _{4.19}
	65.96	34.04	0.43	100.43	MgB _{4.36}
	64.70	34.09	1.10	99.89	MgB _{4.27}
	65.46	34.11	0.62	100.19	MgB _{4.31}
3 (MgB ₂)	43.31	55.53	0.57	99.41	MgB _{1.75}
	44.51	54.46	0.34	99.31	MgB _{1.84}
	82.50	17.46	0.06	100.02	MgB _{10.63}
	82.54	17.15	0^{a}	99.7	MgB _{10.82}
	82.38	17.32	0.1	99.8	MgB _{10.70}
	82.52	17.46	0.05	100.03	MgB _{10.63}
4 (MgB ₂)	48.45	53.88	0.16	102.49	MgB _{2.02}
/	49.59	53.97	0.2	103.76	MgB _{2.07}
	46.21	54.3	0.21	100.73	$MgB_{1.91}$
	48.13	54.0	0.22	102.35	MgB _{2.00}

^a Below detection limit of 160 ppm O.



Fig. 2. Temperature dependence of the magnetic susceptibility of MgB₂ (sample 4).

analyzed by means of the fixed time method of counting at the peak position, the area intensity measurement mode was used for the analysis of B to overcome problems of peak shifts and peak shape alterations. Further details of the analytical procedure were reported in [16]. Typical results of EPMA analysis of some samples are shown in Table 3.

3. Results and discussion

As it is well known, MgB₂ can be formed in a straight forward reaction of appropriate (1:2 or 1:3 molar) stoichiometry of Mg and B at temperatures lower than 865 °C. However traces of MgB₁₂ are detected by EPMA in all of our MgB₂ samples synthesized from the elements. MgB₁₂ was also detected during the early stages of reactions with varying Mg and B compositions (from 1:2 to 1:7) by powder XRD. These findings open grounds for the supposition that this boron-rich compound is always produced first in reactions between magnesium and boron through diffusion of magnesium into the β-rhombohedral boron modification. MgB_{12} is obtained as the main phase at temperatures between 800 and 1000 °C from the reaction of a 1:12 molar ratio of Mg and B. During the past, intercalation compounds of β-rhombohedral boron were reported as $M_x B_{12}$ with M = Li, Cu [25], having similar lattice parameters as MgB₁₂, although structure solution and refinement of this compound have not yet been successfully performed because of the poor peak to background ratio in the XRD powder pattern. A structure refinement based on synchrotron data has been reported for the composition MgB_{20} or rather $Mg_{0.6}B_{12}$, with Mg ions being partially distributed over three distinct crystallographic sites.

DTA examinations have already shown that MgB₂ can be transformed by increase of temperature (610 < T < 862 °C) [26] to yield MgB₄, the next more boron-rich compound in this binary system. When MgB₄ is heated up, it is gradually (655 < T < 881 °C) [26] converted into MgB₇ by further evaporation of magnesium. Finally MgB₇ is converted into MgB₁₂ by arc melting.

All these reactions, involving the temperature-dependent release of magnesium may be regarded as a disadvantage for the straight forward synthesis of MgB₂ from the elements, where elevated temperatures are desired to overcome the slow diffusion in solid state. During our work, we have raised the question whether the reverse reaction, the diffusion of Mg into a higher Mg boride, is possible or not. In course of our reactions, we could show that it is possible to synthesize the metal-rich boride MgB₂ out of MgB₄ or MgB₇. MgB₂ is formed in high yield and good homogeneity from reactions of MgB₄ and Mg at 750 °C, as represented in the Figs. 1 and 3 and corresponding data in Table 3. The magnetic properties of our MgB₂ material is represented in Fig. 2.

In attempt to synthesize MgB_4 by reacting MgB_7 with Mg at 900 °C, this boride is not formed and the reaction product is a mixture of MgB_2 and unreacted MgB_7 . All



Fig. 3. Backscattered electron image of MgB_2 made from MgB_4 and Mg (above) and of the sample prepared directly from the elements (below). MgB_2 (bright phase) forms rims around and veins through MgB_{12} (dark phase).

$$Mg + B \longrightarrow MgB_{12} \longrightarrow MgB_2 \longrightarrow MgB_4 \longrightarrow MgB_7 \longrightarrow MgB_{12}$$

these transformations obtained from reactions in the binary Mg-B system are summarized in Scheme 1.

Electron probe microanalyses (EPMA) were used to examine the compositions of our prepared samples (1-4)for a number of randomly selected spots. Results from these analyses are summarized in Table 3. They show that our MgB₂ sample (4) prepared via MgB₄ are more homogeneous than sample (3) prepared directly from the elements, which are composed of two different phases. These two phases, MgB₂ and Mg deficient MgB₁₂ are represented by the bright and dark areas in the backscattered electron image shown in Fig. 3 (below). The bright area, analyzed as MgB₂, forms rims around and veins through the dark area, which has the composition near MgB₁₂ (Table 3, Fig. 3).

A backscattered electron image of a MgB₂ sample (4) obtained from the reaction of MgB₄ and Mg is shown on top in Fig. 3. The image shows a quite homogeneous (bright) domain of MgB₂ embedded into epoxy resin. The

average elemental ratio in the MgB₂ samples (4) obtained from the reaction of MgB₄ with Mg was found to be Mg_{0.98}B₂ (Table 3). The Rietveld refinement of XRD powder data (Fig. 1) resulted in a Mg deficit as well. The occupancy was found to be 94% (Table 2) which is in good agreement with the EPMA analysis. The deviation from the ideal composition is similar to the findings of other groups who made refinements of MgB₂ from neutron powder data [27] and X-ray data [5].

4. Conclusion

We have shown a new synthesis route for magnesium diboride. With our experiments we were able to demonstrate that the synthesis of MgB₂ from MgB₄ and Mg yields a more homogeneous material than the synthesis from the elements as proven by EPMA and X-ray diffraction. From our studies we conclude the formation of a MgB₁₂-phase as a first step in reactions. If there is enough magnesium present, the formation of MgB₂ starts at temperatures around 650 °C. With increasing temperature the Mg content in the material decreases leading to MgB₄ first and then to MgB₇. At temperatures higher than 1200 °C again a MgB₁₂-phase appears. This behavior is well known. We could show that the decomposition of MgB₂ into Mg and MgB₄ is reversible. This reversibility is the key for a high yield, high quality synthesis of MgB₂. An alternative route for a good quality MgB₂ is the preparation from MgB₇ and Mg that leads also to MgB₂.

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