Increase of the critical current density of MgB₂ superconducting bulk samples by means of methylene blue dye additions

Grivel, Jean-Claude; Rubešová, K.

Published in:
Physica C: Superconductivity and its Applications

Link to article, DOI:
[10.1016/j.physc.2019.1353506](https://doi.org/10.1016/j.physc.2019.1353506)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Grivel, J.-C., & Rubešová, K. (2019). Increase of the critical current density of MgB₂ superconducting bulk samples by means of methylene blue dye additions. *Physica C: Superconductivity and its Applications*, 565, [1353506]. <https://doi.org/10.1016/j.physc.2019.1353506>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/334543692>

Increase of the critical current density of MgB₂ superconducting bulk samples by means of methylene blue dye additions

Article in *Physica C Superconductivity* · July 2019

DOI: 10.1016/j.physc.2019.1353506

CITATION

1

READS

39

2 authors:

Jean-Claude Grivel

Technical University of Denmark

243 PUBLICATIONS 2,442 CITATIONS

SEE PROFILE

Katerina Rubesova

University of Chemistry and Technology, Prague

47 PUBLICATIONS 193 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Ternary oxide phase equilibria [View project](#)

Thermal decomposition studies of metallorganic compounds [View project](#)

Increase of the critical current density of MgB₂ superconducting bulk samples by means of methylene blue dye additions

J.-C. Grivel^{1*} and K. Rubešová²

¹*Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark*

²*University of Chemistry and Technology, Department of Inorganic Chemistry, Technická 5, Prague 6, 166 28, Czech Republic*

Abstract

MgB₂ bulk samples were made by means of reaction of elemental Mg and B powders with or without additions of methylene blue trihydrate, a carbon source, which melts at high temperature upon decomposition. The T_c of the MgB₂ phase as well as its a-axis parameter were decreased as a result of carbon doping, whereas the c-axis parameter only shows a weak tendency for increasing. The critical current density of MgB₂ was improved both in self field and under applied magnetic field for $T \leq 25$ K, the best results being obtained for 0.5 – 1.0 wt.% methylene blue trihydrate addition. Based on normalized flux pinning force ($f(b)$) versus reduced field (b) plots, it was found that the flux pinning mechanism at low reduced field is similar for all samples, with a behavior close to the predictions of the point pinning model. However, for b larger than 1, the behavior of $f(b)$ is significantly altered in the methylene blue trihydrate added samples and tends towards the surface pinning model. Methylene blue trihydrate is an efficient carbon source and furthermore provides a liquid phase between 200°C and 450°C, which may have some influence on the critical current density improvements at low field.

Keywords: MgB₂; doping; carbon; methylene blue; dye

***Corresponding author**

Email: jean@dtu.dk

27 **Introduction**

28 Magnesium diboride (MgB_2), being made of abundant and non-toxic constituent elements, and
29 thanks to its transition temperature (T_c) close to 40 K, is among the most promising superconducting
30 materials for large scale applications. In the form of wires or bulk samples, it has already been used
31 for demonstration units, including high field magnets [1,2], energy storage devices [3,4], high power
32 cables [5], racetrack coils [6], etc. In spite of these successful realizations, further improvements of
33 the critical current density (j_c) performance of MgB_2 wires and bulk samples under the application of
34 magnetic fields are desirable since j_c tends to be severely suppressed when a magnetic field is acting
35 on the material. This is especially important if MgB_2 is meant to be used at an operation temperature
36 of 20 K. One strategy for this purpose consists in the addition of nanoparticles acting as flux pinning
37 centers [7-11]. Carbon doping on the boron sites in the MgB_2 crystal lattice is also known to be
38 effective in enhancing the pinning force and hence the j_c of MgB_2 under high magnetic fields [12-
39 20]. This is in contrast to the general tendency resulting from foreign element doping on the Mg sites
40 [21-26], as well as of Al doping on the B sites [27-31], which induce adverse effects or only limited
41 improvements of the $j_c(B)$ performance due to the influence of these elements on various parameters.
42 Nevertheless, even carbon doping often results in a lowering of the j_c values under self-field and
43 moderate applied magnetic field conditions [14-16,32,33]. Improving the j_c performance of MgB_2
44 samples at high magnetic fields without compromising their properties at lower fields is therefore still
45 an important field of research. Finding carbon sources that also result in the presence of a liquid phase
46 susceptible of acting as a sintering aid before, during or after the formation of MgB_2 may be an
47 interesting strategy as suggested by the positive effect of K_2CO_3 additions on the low and high-field
48 j_c in MgB_2 bulk samples [34].

49 In the present work, the effect of additions of methylene blue trihydrate ($\text{C}_{16}\text{H}_{18}\text{ClN}_3 \cdot 3\text{H}_2\text{O}$) on the
50 formation and some superconducting properties of MgB_2 is reported. This compound is an industrial

dye that is rich in carbon and forms a liquid between 200°C and 450°C when heated in a non-oxidizing atmosphere [35]. Instead of simply evaporating upon melting like e.g. malonic acid [20]. It leaves, at 800°C, a carbonaceous residue amounting to $\approx 37\%$ of its original mass. It has also the advantages of being readily available and inexpensive.

Experimental details

The starting reagents consisted of elemental powders of Mg (Alfa Aesar, 99.8 % purity) and amorphous boron (Aldrich, 95-97 %) as well as methylene blue trihydrate powder with $C_{16}H_{18}ClN_3 \cdot 3H_2O$ composition (Alfa Aesar, assay 100.4 %). The powders were mixed in a mechanical blender (Bachofen, type T2C). Samples with MgB_2 : Methylene blue trihydrate weight ratios of 1 : y with $0.0000 \leq y \leq 0.0125$ with ($\Delta y = 0.0025$) were prepared. A slight excess of B powder (corresponding to 2 at.% of the nominal B stoichiometry) was added to compensate for the impurities, including some Mg, present in the B commercial powder used for the present work, based on a previous optimization study [36]. The mixed powders were pressed into pellets with 12 mm diameter and 1.5 mm thickness under a pressure of 1.8 kbar. The pellets were reacted at 800°C for 1 h under Ar atmosphere with a heating rate of 100°C/h and furnace cooling at the end of the treatment. To avoid oxidation by the residual O_2 (< 0.5 ppm) present in the Ar gas, the pellets were wrapped into Ti foils (Alfa Aesar, 99.7 %, 32 μ m thickness) acting as oxygen getters and at the same time inhibiting Mg evaporation.

After reaction, the pellets were cut with a diamond saw. XRD patterns were recorded in a Bruker X-ray diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) on one piece that was crushed into powder, first without and then again after mixing with silicon powder (Alfa Aesar, 99.999%) used as an internal standard for lattice parameters calculations. These were performed with the UnitCell least square refinement programme [37]. The bulk density (ρ) was estimated by dividing the sample mass by its volume. The microstructure was investigated in a TM3000 table-top scanning electron

75 microscope (SEM) from HITACHI equipped with a QUANTAX 70 EDS analyser, on pieces of each
76 sample composition that were cast into epoxy resin and polished with abrasive suspensions down to
77 0.25 μm particle size. For magnetic measurements, bars with dimensions 8.0 x 2.0 x 1.5 mm^3 were
78 cut in the middle of the reacted pellets. The superconducting critical temperature (T_c) was determined
79 as the mid-point of the diamagnetic transition measured by means of a vibrating sample
80 magnetometer (VSM) in a CRYOGENIC Ltd Mini-CFMS under a magnetic field (B) of 5 mT applied
81 parallel to the longest axis of the samples in zero field cooling conditions. The critical current density
82 (j_c) was calculated using the Bean model from magnetisation hysteresis loops that were recorded on
83 the same samples also with the magnetic field parallel to the long axis. The penetration field (H_p) has
84 been estimated based on the initial magnetization branch of the M-H loops as the applied field at
85 which the M-H dependence departs from a linear relation. The trace element content of the starting
86 boron powder was determined by means of X-ray fluorescence (XRF) measurements with an ARL
87 9400 XP sequential WD-XRF spectrometer equipped with a Rh anode. All peak intensity data were
88 collected in vacuum. The elemental composition of the starting magnesium powder was analysed
89 using X-ray photoelectron spectroscopy (XPS) using ESCAProbe P apparatus (Omicron
90 Nanotechnology Ltd.) with a monochromatized Al anode X-ray source. Step size for survey spectra
91 was 0.5 and 0.2 eV for detail spectra. Size of the analyzed area was approximately 1 mm^2 . 5 keV Ar
92 ions were used for depth profiling. Spectra evaluation was carried out by CasaXPS program.

93 Results

94 Figure 1 contains the XRD patterns of the samples after reaction at 800°C. It can be seen that MgB_2
95 is the majority phase notwithstanding the amount of methylene blue trihydrate added in the starting
96 composition. Besides a little amount of MgO evidenced by a reflection at $2\theta \approx 62.3^\circ$, very low
97 intensity peaks due to unreacted Mg are visible. The intensity of the MgO peak is not significantly
98 increasing with increasing levels of the additive. This is consistent with the relatively low oxygen

99 content of methylene blue trihydrate in comparison with some other additives that have been tested
100 as carbon sources for doping in MgB_2 , e.g. K_2CO_3 [34], malonic acid [20] or succinic acid [38], in
101 which cases the amount of MgO impurity was clearly increasing with doping level. This indicates
102 that the oxygen atoms present in methylene blue trihydrate, which are released below 200°C in the
103 form of water vapor [35], do not react with the Mg powder particles. The presence of MgO in all
104 samples can be partially due to the traces of MgO detected by XPS on the surface of the starting
105 magnesium powder. The a- and c-axis lattice parameters of the MgB_2 phase are plotted in Figure 2
106 and reported in Table 1. The addition of methylene blue trihydrate results in a clear decrease of the
107 a-axis parameter, whereas the c-axis length hardly increases and even this tendency is within the
108 standard deviation. Similar observations use to be reported when carbon is substituted for boron in
109 the MgB_2 lattice [14-16,20,31,34] The variation of the a-axis parameter can be used for estimating
110 the actual amount of carbon that has entered the MgB_2 phase by comparison with the data reported
111 by Lee et al. [39] for a series of C-substituted MgB_2 single crystals. The values, expressed as x in
112 $\text{MgB}_{2-x}\text{C}_x$ for all samples are listed in Table 1 (C_{XRD}), where they can be compared to a theoretical
113 maximum value (C_{nom}) calculated by assuming full substitution of the nominal carbon content in the
114 samples. Both values are rather close, indicating that most of the carbon atoms included in the
115 methylene blue trihydrate additive have been introduced into the MgB_2 lattice. The full width at half
116 maximum (FWHM) of the MgB_2 (002) and (110) XRD peaks were evaluated by fitting to a pseudo-
117 Voigt function. These values are also presented in Table 1. While a slight increase is observed for
118 both as soon as some methylene blue trihydrate is added in the samples, the FWHM remains then
119 constant up to 1 wt.% addition, before starting to increase significantly. Usually, carbon doping in
120 MgB_2 induces a progressive broadening of the XRD reflections [13,16]. In the present case, it seems
121 that some mechanism counterbalances the degradation of crystallinity and/or the increase of residual
122 strain that result from carbon incorporation into the MgB_2 lattice. An effect of the same kind was

123 recently observed for K_2CO_3 additions, although the FWHM even slightly decreased for low additive
124 amounts in that case. Nevertheless, the broadening effect due to carbon substitution becomes
125 preponderant at higher concentrations.

126 SEM images of polished cross-sections of the reacted pellets are shown in Fig.3. The microstructure
127 of the undoped sample is characterized by a matrix made of small ($< 1\ \mu m$) grains consisting of MgB_2
128 (light grey in Fig. 3a) and large, generally elongated lumps (dark grey in Fig 3a). A few grains with
129 low aspect ratio and intermediate grey contrast also appear. These were found to have MgB_7 and
130 MgB_4 compositions respectively. These phases were not detected in the XRD patterns due to the low
131 scattering power of boron. Some elongated cracks can be seen within the MgB_2 matrix (e.g. arrow in
132 Fig. 3a), besides a more refined porosity that can be distinguished as black spots with diameters lower
133 than $3\ \mu m$. In the sample with 0.25 wt.% methylene blue trihydrate addition, the MgB_2 matrix looks
134 denser. In contrast, the large, elongated grain locations are often found to contain hollow areas (Fig.
135 3b). This tendency increases when more methylene blue trihydrate is added in the initial powder
136 mixture and the MgB_2 matrix deteriorates with the development of porosity, which becomes most
137 obvious in the sample with 1.25 wt.% methylene blue trihydrate addition (Fig. 3f). Methylene blue
138 trihydrate forms a molten phase between $200^\circ C$ and $450^\circ C$, and releases about 40% of its mass in the
139 form of gaseous species in the same temperature interval [35]. Antagonist effects are expected from
140 these two phenomena. Gas evolution tends to induce porosity, whereas a liquid phase is likely to
141 increase the bulk ceramic density by filling pores. The SEM micrographs indicate that the latter effect
142 plays a major role for large amounts of additive. In contrast, the beneficial effect of the liquid phase
143 towards increasing the bulk density seems preponderant at low addition levels, as further illustrated
144 by the slight increase of ρ for 0.25 to 1.00 wt.% addition (Table 1). The somehow lower ρ value for
145 the 0.50 wt.% sample compared to the 0.25 and 0.75 wt.% samples could simply be due to a little
146 difference in the initial packing density.

Besides C, H and O, methylene blue trihydrate also contains N, S and Cl. Elemental analysis was performed by means of EDS on the polished cross section of the sample with 1.25 wt.% additive to check for the presence of these three elements after reaction. The results of a large area measurement (2 mm²) reveal that N is absent from this sample, indicating that it has been lost during the reaction process. In contrast, Cl can be identified, meaning that a part at least of the initial content of this element is still present. This is an interesting observation considering the fact that the thermal decomposition residue of methylene blue at 800°C contains some N beside C but no Cl, the latter element escaping below 300°C in the form of HCl [35]. This means that HCl is likely to react with either Mg or B to trap the chlorine atoms up to 800°C. The most probable mechanism is a reaction with Mg in the form of MgO that is present in the starting Mg powder [40]. Moreover, boron halides are not thermally stable enough to be formed at a temperature of 800°C. The location of Cl in the microstructure could unfortunately not be identified due to its low amount. Attempts at doping Cl in MgB₂ haven't been reported so far, so that it is difficult to estimate its contribution to the evolution of the lattice parameters and superconducting properties of MgB₂ in case Cl is actually introduced in the lattice. However, since the C:Cl atomic ratio in methylene blue trihydrate is 16:1, it can be assumed that Cl does not play a significant role compared to the effect of C doping. The EDS spectrum in Fig.4 (inset) shows a few other peaks emerging from the background. The presence of Ca, K, Si and Fe can be traced back to the impurities present in the starting Mg powder (for Ca) and B powder (for Si, K and Fe), with levels corresponding to 300, 880 ppm, 2770 ppm and 250 ppm at.% respectively. Concerning the traces of sulfur revealed by the EDS spectrum, its origin is unclear. It may be a remnant of the methylene blue trihydrate decomposition or come from the Mg precursor powder (300 ppm). Its amount in the B powders is however negligible.

Magnetic susceptibility data around the superconducting transition, measured in zero field cooling mode, are plotted in Figure 5 for all samples after normalization to the magnetization value at 5 K.

171 T_c , also reported in Table 1, decreases monotonously with the increase of the methylene blue addition
172 level. Following again the data published by Lee et al. [39], the T_c of the samples can be used to
173 estimate the amount of carbon doped in the MgB_2 phase. The values are listed in Table 1 (C_{Tc}) and
174 confirm those that were estimated based on the a-axis parameter variations and are thus again close
175 to the maximum substitution level possible considering the nominal C content available in the
176 methylene blue trihydrate additive (C_{nom}). This allows concluding that methylene blue trihydrate is
177 an efficient carbon source as nearly all the carbon is doped into the superconductor. The overall
178 reaction taking place in the powder mixture is however difficult to determine in view of the intricate
179 thermal decomposition process of methylene blue trihydrate and because its potential interactions, as
180 well as those of its decomposition products, with Mg or B are not known.

181 The occurrence of a liquid phase between 200°C and 450°C [35] can help ensuring the homogeneous
182 distribution of C in the samples. Thus the increase of the FWHM of the MgB_2 XRD peaks, which
183 usually results from C doping, is minimized at least for the lowest doping levels. Inhomogeneous
184 distribution of carbon in MgB_2 tends to increase the superconducting transition width [41]. The
185 suppression of ΔT_c increase for low initial methylene blue trihydrate contents (Table 1) also indicates
186 a good homogeneity of carbon distribution in the MgB_2 matrix.

187 Figure 6 shows the $j_c(B)$ dependence calculated from magnetization hysteresis loops using the Bean
188 model on all samples for measurements conducted at 35 K, 30 K, 25 K, 20 K and 15 K. At 35 K, i.e.
189 rather close to T_c for the compositions with the highest methylene blue trihydrate initial content, j_c is
190 lower in all doped samples. However, at 30 K, the samples with 0.25 and 0.50 wt.% methylene blue
191 trihydrate already have a higher low field j_c than the pure sample, which however still exhibits better
192 performance above 0.7 T. At lower temperatures, the j_c of the samples with methylene blue trihydrate
193 additions tends to become significantly higher by comparison with that of the undoped sample. The

194 best j_c performance is observed in the $x = 0.50$ wt.% sample at 25 K, but at lower temperatures 1.00
 195 wt.% addition yields the best results.

196 The pinning force ($F_p = j_c \cdot B$) is plotted in Fig.7 for measurements performed at 30 K and 20 K. The
 197 $F_p(B)$ data for 35 K, 25 K and 15 K can be seen in Fig.S2. The behavior of $F_p(B)$ is qualitatively
 198 similar to that of $j_c(B)$. For T close to T_c , $F_p(B)$ is larger in the undoped sample for the whole applied
 199 magnetic field range. However, below 30 K, the $F_p(B)$ of the doped samples becomes clearly higher
 200 than without methylene blue trihydrate additions. Here again, the sample with 0.50 wt.% addition
 201 shows the highest value at 25 K but is superseded by the sample with 1.00 wt.% at lower temperatures.

202 The normalized pinning force ($f = F_p/F_{pmax}$), i.e. the pinning force $F_p(B)$ normalized by the
 203 maximum value of $F_p (= F_{pmax})$ is shown in Fig.8 for all samples at 30 K and 20 K as a function of b
 204 $= B/B_{Fpmax}$ i.e. the applied magnetic field B normalized by the field corresponding to F_{pmax} . The $f(b)$
 205 data for measurements conducted at 35 K, 25 K and 15 K can be found in Fig.S3. The models
 206 corresponding to surface pinning (1), normal point pinning (2) and $\Delta\kappa$ pinning (3) [42] were used to
 207 evaluate the data and gain some insight into the dominant flux pinning mechanisms at play in the
 208 samples:

$$209 \quad f(b) = \frac{25}{16} \sqrt{b} \left(1 - \frac{b}{5}\right)^2 \quad (1)$$

$$210 \quad f(b) = \frac{9}{4} b \left(1 - \frac{b}{3}\right)^2 \quad (2)$$

$$211 \quad f(b) = 3b^2 \left(1 - \frac{2b}{3}\right) \quad (3)$$

212 In the low applied magnetic field range, i.e. $b \leq 1$, all $f(b)$ curves are superimposed and hence
 213 demonstrate a similar flux pinning behavior notwithstanding of temperature or composition. The
 214 experimental data are situated between the predictions of the point pinning and $\Delta\kappa$ pinning models,
 215 so that it may be deduced that both types of pinning contribute to the observed $f(b)$ dependence.
 216 However, point pinning seems to account for the largest contribution. In contrast, for $f(b) > 1$, the
 217 addition of methylene blue trihydrate results in a shift towards the surface pinning behavior, which
 218 however becomes less pronounced as the temperature decreases, so that at 15 K all samples behave
 219 in a similar way again. An upwards shift of the $f(b)$ curves at $b > 1$ has already been observed several
 220 times in relation to carbon doping in MgB_2 [19,34,43-46]. The fact that this effect tends to be
 221 cancelled at low temperatures was not mentioned earlier. **One may however question the conclusion**
 222 **that the upwards shift of the $f(b)$ curves above $b = 1$ for T close to T_c really reflects a change in the**
 223 **flux pinning mechanism. In fact, as the applied field approaches the irreversibility field, the induced**
 224 **superconducting current may not flow around the whole circumference of the sample anymore. Since**
 225 **the sample size was assumed to be the length scale of the induced current for all measurement**
 226 **conditions, $j_c(B)$ and thus $F(B)$ as well as $f(b)$ may not be accurately estimated at the highest**
 227 **temperatures and/or fields thereby leading to artefacts. Since j_c depends on H, the application of the**
 228 **Bean model is in general only valid for H larger than the penetration field (H_p). For $H < H_p$, j_c will be**
 229 **overestimated, especially when the field is applied parallel to the long axis of the sample [47]. This**
 230 **effect might be significant for the analysis of the normalized F_p data at $b < 1$ if H_p is close to B_{Fpmax} .**
 231 **The H_p values for all samples at various temperatures are listed in Table S1. Although they are larger**
 232 **than those previously reported for MgB_2 single crystals [48], comparison with the F_p versus B data**
 233 **in Fig.7 and Fig.S2 show that they are significantly lower than B_{Fpmax} for all samples and**
 234 **temperatures. The influence of this effect on the analysis of the flux pinning mechanism at $b < 1$ is**
 235 **therefore limited to the very beginning of the $f(b) - b$ curves and does not invalidate the conclusions.**

236 While methylene blue trihydrate additions have a beneficial influence on j_c in self field, contrary to
237 many other carbon doping sources, it has no influence on the flux pinning mechanism under low
238 applied fields, even if the absolute value of F_p is increased. This shows that the low-field and self-
239 field j_c enhancement is not due to fundamental modifications of the flux pinning landscape. The fact
240 that methylene blue trihydrate forms a molten phase between 200°C and 450°C might be playing a
241 role. Although solidification of the solid residue takes place well below the onset temperature of
242 MgB_2 formation [49], a transient liquid phase can act on the microstructure of the Mg – B powder
243 mixture during the temperature ramp up. A similar effect was assumed for explaining the effect of
244 K_2CO_3 additions [34] but in the present case the self-field j_c increase at 15 K reaches 22 % versus 12
245 % for K_2CO_3 . A liquid phase forming at relatively low temperatures acts differently from metallic
246 additives that induce melting in contact with Mg due to the occurrence of an eutectic structure in
247 some binary phase diagrams [50-57], in which case the liquid is present during the MgB_2 formation
248 process. A prospective route for further improving the superconducting performance of MgB_2 could
249 consist in combining additives that may result in carbon doping while transient liquid phases are
250 available during temperature ramp up and while the MgB_2 phase is forming.

251 **Conclusions**

252 The present results demonstrate that methylene blue trihydrate ($\text{C}_{16}\text{H}_{18}\text{ClN}_3 \cdot 3\text{H}_2\text{O}$), a cheap and
253 readily available chemical used as an industrial dyestuff, is an efficient source of carbon atoms in
254 view of doping in the MgB_2 lattice using the in-situ synthesis route as approximately all the carbon
255 atoms from methylene blue trihydrate end up in the MgB_2 phase considering lattice parameters and
256 T_c variations. While the carbon atoms originating from the additive are introduced in MgB_2 , nitrogen
257 was not detected by EDS measurements after reaction. On the other hand, some sulfur and chlorine
258 were found, although at a trace impurity level so that their exact location in the sample could not be
259 ascertained. Nevertheless, since no report dealing with sulfur or chlorine doping in MgB_2 seem to

260 have been published yet, it would be interesting to investigate their possible individual effects as they
261 might be incorporated in the lattice of the superconducting phase. At 35 K, the $j_c(B)$ performance of
262 the undoped sample as well as its pinning force are the highest. However, doping induces clear
263 improvements for $T < 30$ K, with the best results achieved for 1.00 wt.% methylene blue trihydrate
264 addition, an amount that is at least one order of magnitude smaller than for most other organic
265 compounds reported as carbon sources up to now. Attempts at using methylene blue trihydrate as an
266 additive for manufacturing MgB_2 wires could be interesting, however in that case, it would be
267 recommended to start from dehydrated methylene blue to avoid possible adverse effects during H_2O
268 release inside the metallic sheath.

269 **Acknowledgements**

270 Mr. Henrik Paulsen is gratefully acknowledged for preparing the polished cross-sections of the
271 samples for SEM investigations.

272

273

274 **References**

- 275 [1] D.A. Abin, N.A. Mineev, M.A. Osipov, S.V. Pokrovskii and I.A. Rudnev, Dry cryomagnetic
276 system with MgB₂ coil, J, Phys. Conf. Ser. 941 (2017) 012056
- 277 [2] J. Liu, H. Ma, L. Huang and P. Ju, Research on an axial Maglev device with primary
278 superconductive coils for a 1000 MW hydraulic generator set, IEEE Trans. Appl. Supercond. 27
279 (2017) 5000106
- 280 [3] S. Mizuno, T. Yagai, T. Okubo, S. Mizuochi, M. Kamibayashi, M. Jinbo, T. Takao, Y. Makida,
281 T. Shintomi, N. Hirano, T. Komagome, K. Tsukada, Y. Onji, Y. Arai, M. Tomita, D. Miyagi, M.
282 Tsuda and T. Hamajima, Feasibility study of MgB₂ cable for pancake coil of energy storage device,
283 IEEE Trans. Appl. Supercond. Accepted for publication, DOI 10.1109/TASC.2018.2794334
- 284 [4] A. Morandi, A. Anemona, G. Angeli, M. Breschi, A. Della Corte, C. Ferdeghini, C. Gandolfi, G.
285 Grandi, G. Grasso, L. Martini, U. Melaccio, D. Nardelli, P.L. Ribani, S. Siri, M. Troppeano, S. Turtù
286 and M. Vignolo, The DRYSMES4GRID project: Development of a 500 kJ/200 kW cryogen-free
287 cooled SMES demonstrator based on MgB₂, IEEE Trans. Appl. Supercond. 28 (2018) 5700205
- 288 [5] K. Konstantopoulou, A. Ballarino, A. Gharib, A. Stimac, M. Garcia Gonzalez, A.T. Perez
289 Fontenla and M. Sugano, Electro-mechanical characterization of MgB₂ wires for the superconducting
290 link project at CERN, Supercond. Sci. Technol. 29 (2016) 084005
- 291 [6] F. Karaboga, H. Yetis, M. Akdogan, D. Gajda and I. Belenli, Design, fabrication, and testing of
292 MgB₂/Fe racetrack coil, IEEE Trans. Appl. Supercond. 28 (2018) 6200805
- 293 [7] J. Wang, Y. Bugoslavsky, A. Berenov, L. Cowey, A.D. Caplin, L.F. Cohen, L.D. Cooley, X. Song
294 and D.C. Larbalestier, High critical current density and improved irreversibility field in bulk MgB₂
295 made by a scalable, nanoparticle addition route, Appl. Phys. Lett. 81 (2002) 2026 – 2028
- 296 [8] G.J. Xu, J.-C. Grivel, A.B. Abrahamsen and N.H. Andersen, Enhancement of the irreversibility
297 field in bulk MgB₂ by TiO₂ nanoparticle addition, Physica C 406 (2004) 95 - 99

298 [9] E. Babic, N. Novosel, D. Pajic, S. Galic, K. Zadro and D. Drobac, Magnetic nanoparticles in
 299 MgB_2 : vortex pinning, pair breaking and connectivity, *J. Magn. Magn. Mater.* 400 (2016) 88 – 92

300 [10] D. Goto, T. Machi, Y. Zhao, N. Koshizuka, M. Murakami and S. Arai, Improvement of critical
 301 current density in MgB_2 by Ti, Zr and Hf doping, *Physica C* 392 (2003) 272 - 275

302 [11] N. Novosel, S. Galic, D. Pajic, K. Zadro and E. Babic, Enhancing superconducting properties of
 303 MgB_2 by addition of magnetic particles, *J. Supercond. Nov. Magn.* 28 (2015) 425 – 430

304 [12] M.G. Babaoglu, S. Safran, Ö.Civek, H. Ail, E. Ertekin, Md. Shahriar, A. Hossein, E. Yanmaz
 305 and A. Gencer, Microstructural and superconducting properties of C_6H_6 added bulk MgB_2
 306 superconductor, *J. Magn. Magn. Mater.* 324 (2012) 3455 – 3459

307 [13] S.X. Dou, O. Shcherbakova, W.K. Yeoh, J.H. Kim, S. Soltanian, X.L. Wang, C. Senatore, R.
 308 Flükiger, M. Dhallo, O. Husnjak and E. Babic, Mechanism of enhancement in electromagnetic
 309 properties of MgB_2 by nano SiC doping, *Phys. Rev. Lett.* 98 (2007) 097002

310 [14] S. Soltanian, J. Horvat, X.L. Wang, P. Munroe and S.X. Dou, Effect of nano-carbon particle
 311 doping on the flux pinning properties of MgB_2 superconductor, *Physica C* 390 (2003) 185 – 190

312 [15] C.H. Cheng, H. Zhang, Y. Zhao, Y. Feng, X.F. Rui, P. Munroe, H.M. Zeng, N. Koshizuka and
 313 M. Murakami, Doping effect of nano-diamond on superconductivity and flux pinning in MgB_2 ,
 314 *Supercond. Sci. Technol.* 16 (2003) 1182 – 1186

315 [16] J.M. Parakkandy, M. Shahabuddin, M. Shahabuddin Shah, N.S. Alzayed, S.A.S. Qaid, N.M.
 316 Ramay and M.A. Shar, Effect of glucose doping on the MgB_2 superconductors using cheap crystalline
 317 boron, *Physica C* 519 (2015) 137 – 141

318 [17] L.B.S. Da Silva, A.A. Vianna, A.L.R. Manesco, E.E. Hellstrom and D. Rodrigues Jr., The
 319 influence of stearic acid addition on the superconducting properties of MgB_2 , *IEEE Trans. Appl.*
 320 *Supercond.* 26 (2016) 7100204

321 [18] J.H. Kim, S.X. Dou, M.S.A. Hossain, X. Xu, J.L. Wang, D.Q. Shi, T. Nakane and H. Kumakura,
322 Systematic study of a $\text{MgB}_2 + \text{C}_4\text{H}_6\text{O}_5$ superconductor prepared by the chemical solution route,
323 Supercond. Sci. Technol. 20 (2007) 715 - 719

324 [19] Z. Gao, Y. Ma, X. Zhang, D. Wang, Z. Yu, K. Watanabe, H. Yang and H. Wen, Strongly
325 enhanced critical current density in MgB_2/Fe tapes by stearic acid and stearate doping, Supercond.
326 Sci. Technol. 20 (2007) 485 – 489

327 [20] C. Li, H. Suo, M. Liu, L. Ma, Y. Wang, M. Tian, B. Wan, J. Cui and Y. Ji, Effect of malonic
328 acid and of different doping methods on the superconducting properties of MgB_2 superconductors,
329 Physica C 555 (2018) 60 - 65

330 [21] J.-C. Grivel, Influence of iridium doping in MgB_2 superconducting wires, Physica C 547 (2018)
331 7 - 15

332 [22] Y. Zhao, C. Ke, Y. Yang, C.C. Hsieh, D. Zhou, C. Cheng and Y. Zhang, CrB_2 doping effects on
333 critical current density and flux pinning of MgB_2 , IEEE Trans. Appl. Supercond. 29 (2019) 6200305

334 [23] J.-C. Grivel, A. Alexiou, S. Namazkar and A. Pitillas, Effect of platinum group metal doping in
335 magnesium diboride wires, IEEE Trans. Appl. Supercond. 26 (2016) 6200505

336 [24] J.-C. Grivel, S. Namazkar, A. Alexiou and O.J. Holte, Preparation and characterization of Os
337 doped MgB_2 , Physica C 507 (2014) 70 - 74

338 [25] J.C. Grivel and M. Burdusel, Preparation and characterization of Sc doped MgB_2 wires, Physica
339 C 528 (2016) 65 – 72

340 [26] C.H. Cheng, Y. Yang, C. Ke and H.T. Lin, Iron doping effect on superconducting properties of
341 MgB_2 , Physica C 470 (2010) 1092 - 1095

342 [27] B. Kang, M.-S. Park, H.-S. Lee, M.-H. Jung and S.-I. Lee, Comparison between Al and C
343 substitutions in the upper critical field of MgB_2 single crystals, J. Kor. Phys. Soc. 58 (2011) 498 - 502

344 [28] J.Y. Xiang, D.N. Zheng, J.Q. Li, S.L. Li, H.H. Wen and Z.X. Zhao, Effects of Al doping on the
 345 superconducting and structural properties of MgB_2 , *Physica C* 386 (2003) 611-615
 346 [29] G.J. Xu, J.-C. Grivel, A.B. Abrahamsen, X.P. Chen and N.H. Andersen, Structure and
 347 superconductivity of double-doped $\text{Mg}_{1-x}(\text{Al}_{0.5}\text{Li}_{0.5})_x\text{B}_2$, *Physica C* 399 (2003) 8-14
 348 [30] G.J. Xu, J.-C. Grivel, A.B. Abrahamsen, X.P. Chen and N.H. Andersen, Superconducting
 349 properties of Zn and Al double-doped $\text{Mg}_{1-x}(\text{Zn}_{0.5}\text{Al}_{0.5})_x\text{B}_2$, *Physica C* 403(2004) 113-118
 350 [31] A.Yu. Potanin, D.Yu. Kovalev, E.A. Levashov, P.A. Loginov, E.I. Patsera, N.V. Shvyndina,
 351 K.S. Pervakov, V.A. Vlasenko and S.Yu. Gavrilkin, The features of combustion synthesis of
 352 aluminium and carbon doped magnesium diboride, *Physica C* 541 (2017) 1 – 9
 353 [32] C. Laliena, E. Matínez, L. A. Angurel and R. Navarro, Effect of ball milling and fatty acid
 354 addition on the properties of MgB_2 wires, *IEEE Trans. Appl. Supercond.* 25 (2015) 6200204
 355 [33] D.N. Rakov, A.E. Vorobieva, P.V. Konovalov, E.V. Kotova, Yu.N. Belotelova and M.V.
 356 Polikarpova, Influence of carbon doping on MgB_2 superconducting properties, *Physics Proc.* 36
 357 (2012) 1480 - 1485
 358 [34] J.-C. Grivel, Critical current density improvements in MgB_2 superconducting bulk samples by
 359 K_2CO_3 additions, *Physica C* 550 (2018) 1 – 6
 360 [35] J.-C. Grivel, Thermal stability and decomposition of methylene blue trihydrate, In preparation
 361 [36] J.C. Grivel, A. Alexiou, K. Rubešová, X. Tang, N.H. Andersen, M. von Zimmermann and A.
 362 Watenphul, Preparation and characterization of $\text{Mg}_{1-x}\text{B}_2$ bulk samples and Cu/Nb sheathed wires with
 363 low grade amorphous boron powder, *J. Supercond. Nov. Magn.* 27 (2014) 497-504
 364 [37] T.J.B. Holland and S.A.T. Redfern, Unit cell refinement from powder diffraction data: The use
 365 of regression diagnostics, *Mineral. Mag.*, 61 (1997) 65-77.

366 [38] H. Agil, O. Cicek, E. Ertekin, A. Motaman, M.S.A. Hossain, S.X. Dou and A. Gencer, Effects
 367 of MgO on the electronic and superconducting properties in succinic acid ($C_4H_6O_4$) doped MgB_2
 368 bulks, J. Supercond. Nov. Magn. 26 (2013) 1525 - 1529
 369 [39] S. Lee, M. Takahiko, A. Yamamoto, H. Uchiyama and S. Tajima, Carbon-substituted MgB_2
 370 single crystals, Physica C 397 (2003) 7 – 13
 371 [40] Z. Zhang, X. Lu, S. Yang and F. Pan, Preparation of anhydrous magnesium chloride from
 372 magnesite, Industrial & Engineering Chemistry Research 51 (2012) 9713 - 9718
 373 [41] C. Senatore, P. Lezza, R. Lortz, O. Shcherbakova, W.K. Yeoh, S.X. Dou and R. Flükiger,
 374 Specific heat and magnetic relaxation analysis of MgB_2 bulk samples with and without additives,
 375 IEEE Trans. Appl. Supercond. 17 (2007) 2941 – 2944
 376 [42] T. Goto, K. Inagaki and K. Watanabe, Critical current density in filamentary (Nd, Sm, Eu, Gd)
 377 – Ba – Cu – O superconductors prepared by a solution spinning method, Physica C 330 (2000) 51 –
 378 57
 379 [43] S. Ueda, J.-I. Shimoyama, A. Yamamoto, S. Horii and K. Kishio, Enhanced critical current
 380 properties observed in Na_2CO_3 -doped MgB_2 , Supercond. Sci. Technol. 17 (2004) 926 – 930
 381 [44] J.L. Wang, R. Zeng, J.J. Kim, L. Lu and S.X. Dou, Effects of C substitution on the pinning
 382 mechanism of MgB_2 , Phys. Rev. B 77 (2008) 174501
 383 [45] S.R. Ghorbani, M. Darini, X.L. Wang, M.S.A. Hossain and S.X. Dou, Vortex flux pinning
 384 mechanism and enhancement of in-field j_c in succinic acid doped MgB_2 , Sol. State Comm. 168
 385 (2013) 1 - 5
 386 [46] C.D. Wang, D.L. Wang, X.P. Zhang, C. Yao, C.L. Wang and Y.W. Ma, Aniline doping and high
 387 energy milling to greatly enhance electromagnetic properties of magnesium diboride
 388 superconductors, Physica C 489 (2013) 36 – 39

389 [47] A. Sanchez and C. Navau, Critical-current density from magnetization loops of finite high- T_c
390 superconductors, *Supercond. Sci. Technol.* 14 (2001) 444 - 447

391 [48] A.D. Caplin, Y. Bugoslavsky, L.F. Cohen, L. Cowey, J. Driscoll, J. Moore and G.K. Perkins,
392 Critical fields and critical currents in MgB_2 , *Supercond. Sci. Technol.* 16 (2003) 176 - 182

393 [49] J.-C. Grivel, R. Pinholt, N.H. Andersen, P. Kovac. I. Husek and J. Homeyer, In situ investigations
394 of phase transformations in Fe-sheathed MgB_2 wires, *Supercond. Sci. Technol.* 19 (2006) 96 - 101

395 [50] Y. Hishinuma, A. Kikuchi, K. Matsuda, K. Nishimura, Y. Kubota, S. Hata, S. Yamada and T.
396 Takeuchi, Microstructure and superconducting properties of Cu addition MgB_2 multifilamentary
397 wires using boron isotope powder as the boron source material, *Physics Procedia* 36 (2012) 1486-
398 1491

399 [51] J.-C. Grivel, Attempts at doping indium in MgB_2 , *Physica C* 531 (2016) 67 - 71

400 [52] P. Badica, G. Aldica, M. Burdusel and K. Endo, Composites of MgB_2 with Bi_2O_3 , Bi, Sb_2O_3 , or
401 Sb obtained by ex-situ spark plasma sintering, *Jpn. J. Appl. Phys.* 51 (2012) 11PG13

402 [53] D. Batalu, G. Aldica, S. Popa, L. Miu, M. Enculescu, R.F. Negrea, I. Pasuk and P. Badica, High
403 magnetic field enhancement of the critical current density by Ge, GeO_2 and $Ge_2C_6H_{10}O_7$ additions to
404 MgB_2 , *Scripta Materialia* 82 (2014) 61 – 64

405 [54] J. Huo, Y.C. Liu, Z.Z. Dong and H. Jiang, Effect of Sn-doping on the sintering process of MgB_2
406 and its superconductive properties, *J. Mater. Sci. Mater. Electron.* 22 (2011) 233 – 237

407 [55] M. Kuhberger and G. Gritzner, Effects of Sn, Co and Fe on MgB_2 , *Physica C* 370 (2002) 39 - 43

408 [56] J.-C. Grivel, A. Abrahamsen and J. Bednarčik, Effects of Cu or Ag additions on the kinetics of
409 MgB_2 phase formation in Fe-sheathed wires, *Supercond. Sci. Technol.* 21 (2008) 035006

410 [57] J.-C. Grivel, N.H. Andersen, P.G.A.P. Pallewatta, Y. Zhao and M.v. Zimmermann, Influence of
411 Bi, Se and Te additions on the formation temperature of MgB_2 , *Supercond. Sci. Technol.* 25 (2012)
412 015010

413 **Figure captions**

414 **Figure 1:** XRD patterns of the samples after reaction at 800°C. The amount of methylene blue
415 trihydrate addition is indicated in wt.% above the respective patterns. The Miller indices denote MgB₂
416 diffraction peaks. ● : MgO, ◆ Mg.

417 **Figure 2:** Lattice parameters of the MgB₂ phase versus nominal methylene blue trihydrate content.

418 **Figure 3:** SEM images (backscattering mode) of polished cross-sections of the samples with nominal
419 methylene blue trihydrate contents equal to 0.00 wt. % (a); 0.25 wt. % (b); 0.50 wt. % (c), 0.75 wt.
420 % (d), 1.00 wt.% and 1.25 wt. % (e), after reaction at 800°C. The same magnification was used for
421 all images. The arrow in (a) shows an elongated crack.

422 **Figure 4:** EDS spectrum obtained from the polished cross-section of the sample with 1.25 wt.%
423 nominal methylene blue trihydrate content. The inset shows a detail of the same spectrum.

424 **Figure 5:** VSM data showing the superconducting transition in reacted samples with various nominal
425 methylene blue trihydrate contents.

426 **Figure 6:** Critical current density (j_c) at 35 K, 30 K, 25 K, 20 K and 15 K versus applied magnetic
427 field (B) calculated with the Bean model using magnetization hysteresis loops. The nominal
428 methylene blue trihydrate content is indicated as wt.%.

429 **Figure 7:** Pinning force (F_p) at 30 K and 20 K versus applied magnetic field (B) for samples with
430 various nominal methylene blue trihydrate contents indicated as wt.%.

431 **Figure 8:** Normalized pinning force $f = F_p/F_{pmax}$ at 30 K and 20 K versus the normalized magnetic
432 field $b = B/B_{Fpmax}$. The data for the different nominal methylene blue trihydrate contents indicated as
433 wt.%. are compared to theoretical predictions of three flux pinning mechanism models: surface
434 pinning (S), point pinning (P) and $\Delta\kappa$ pinning (K).

435

436

437 **Table captions**

438 **Table 1:** *a*-axis and *c*-axis lattice parameters; bulk density (ρ), critical temperature (T_c) and transition
439 width (ΔT_c) (10% - 90% of the maximum diamagnetic signal); full width at half maximum (FWHM)
440 of the MgB₂ (002) and (110) X-ray diffraction peaks; carbon content estimated from XRD data (C_{XRD})
441 and T_c values (C_{Tc}) as well as theoretical maximum carbon doping level (C_{nom}) of the MgB₂ + x
442 C₁₆H₁₈ClN₃·3H₂O samples after heat treatment at 800°C.

443

444

445

446

447

448

Figure 1

Figure 2

461
462
463
464

465
466
467
468

Figure 3

Figure 4

normalized magnetic susceptibility

Figure 5

Figure 6

Figure 7

Figure 8

Methylene Blue [wt.%]	a [Å]	c [Å]	ρ [g/cm ³]	T _c [K]	ΔT_c [K]	FWHM ₍₀₀₂₎ [°] (2 θ)	FWHM ₍₁₁₀₎ [°] (2 θ)	C _{XRD} [Expressed as x in MgB _{2-x} C _x]	C _{Tc}	C _{nom}
0.00	3.0851(3)	3.5223(4)	1.21(2)	38.63(5)	0.60(8)	0.296(5)	0.346(6)	0.000	0.000	0.000
0.25	3.0839(3)	3.5225(4)	1.32(2)	38.24(5)	0.65(9)	0.308(5)	0.382(8)	0.008(3)	0.005(2)	0.005
0.50	3.0826(2)	3.5229(3)	1.26(2)	38.07(5)	0.58(8)	0.304(5)	0.385(8)	0.010(3)	0.008(3)	0.011
0.75	3.0812(3)	3.5227(4)	1.35(2)	37.66(5)	0.65(9)	0.309(5)	0.388(6)	0.016(3)	0.014(4)	0.016
1.00	3.0798(3)	3.5231(4)	1.29(2)	36.94(5)	0.64(9)	0.308(5)	0.382(8)	0.023(3)	0.024(4)	0.022
1.25	3.0793(3)	3.5229(4)	1.13(2)	36.50(5)	0.76(9)	0.350(6)	0.441(6)	0.026(3)	0.030(4)	0.027

Table 1

Supplementary Material

Increase of the critical current density of MgB₂ superconducting bulk samples by means of methylene blue dye additions

J.-C. Grivel^{1*} and K. Rubešová²

¹*Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark*

²*University of Chemistry and Technology, Department of Inorganic Chemistry, Technická 5, Prague 6, 166 28, Czech Republic*

MgB₂ grain size

Figure S1 shows an SEM image (5000 x magnification), where various types of phases are visible. The large, elongated grains consist of MgB₇, the grey particles with diameter up to 2 μm are made of MgB₄, the small white grains are SiC particles remaining from the grinding pastes and the finally the MgB₂ grains form the light grey matrix. The size of the MgB₂ grains can be estimated as 1 – 3 μm based on areas, where individual particles are distinguishable. Similar microstructures were observed for all samples.

Figure S1: SEM image (backscattering mode) of the undoped sample after reaction.

Figure S2: Pinning force (F_p) at 35 K, 25 K and 15 K versus applied magnetic field (B) for samples with various nominal methylene blue trihydrate contents indicated as wt.%.

Figure S3: Normalized pinning force $f(b) = F_p/F_{pmax}$ at 35 K, 25 K and 15 K versus the normalized magnetic field $b = B/B_{pmax}$. The data for the different nominal methylene blue trihydrate contents indicated as wt.% are compared to theoretical predictions of three flux pinning mechanism models: surface pinning (S), point pinning (P) and $\Delta\kappa$ pinning (K).

Doping level (x)	35 K	30 K	25 K	20 K	15 K
0.00	158	253	289	341	440
0.25	139	249	281	357	440
0.50	128	223	273	328	420
0.75	109	241	271	305	420
1.00	86	209	260	284	415
1.25	67	179	177	233	397

Table S1: H_p values in mT for all samples at various temperatures. The uncertainty on all values is of +/- 10%.