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High pressure synthesized magnesium diboride- and dodecaboride-based superconductors: structure and properties

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Abstract. The critical current density, j_c, of high-pressure synthesized MgB_2-based balk materials correlates with the amount and distribution of higher borides (MgB_{12}) and Mg-B-O inclusions, which in tern correlates with the synthesis temperature and presence of additions (Ti, Ta, SiC). High-pressure-synthesized materials with near MgB_{12} composition of matrix exhibited superconducting transition temperature, T_c, of about 37 K, rather high j_c ($5 \cdot 10^5$ and 10^3 A/cm^2 in 0 T and 3.5 T, respectively, at 20 K) and doubled matrix microhardness: 25±1.1 GPa at 4.9 N –load as compared to materials with MgB_2).

Introduction

Superconductive nanostructural MgB_2-based materials with high critical current densities, high fields of irreversibility, hardness, fracture toughness, and Young modulus, which can trap high magnetic fields, may be efficiently used in cryogenic technique, in particular in electromotors, cryogenic pumps, fault current limiters, magnetic bearings, fly-wheel energy storage devices, MAGLEV transport, magnetron-sputtering devices, etc. operating at liquid hydrogen temperatures.

Using high-pressure techniques to manufacture MgB_2 we can surpass the evaporation of magnesium during the manufacturing process and obtain a material with near theoretically dense structure, high critical currents and mechanical characteristics. High-pressure apparatuses with a volume of 330 cm^3 allow us to produce blocks of more than 60 mm in diameter and 20 mm thick at 2 GPa pressure.

It has been established in our previous study that superconductive properties of MgB_2 depend on the amount, size and distribution of higher borides inclusions (the finer the MgB_{12} inclusions and the larger amount of them, the higher j_c) [1]. Besides, it has been shown that additions of Ti, Ta, and Zr can essentially improve j_c of high-pressure high-temperature synthesized MgB_2 [2-5], but we observed absolutely different mechanism of their influence than that proposed for materials synthesized under pressureless conditions. In the case that Ti or Zr is added the improvement in

critical current density in materials synthesized at ambient pressure is usually explained by the formation of TiB_2 or ZrB_2 thin layers or inclusions at grain boundaries that increase the number of pinning centers, which is ascribed to a j_c improvement caused by doping with these elements [6].. In the case of high-pressure synthesized MgB_2 the Ti-, Zr- or Ta-containing inclusions are rather coarse and too randomly distributed in material matrix to be pinning centers by themselves or to refine the MgB_2 structure. Under high-pressure conditions Zr, Ti or Ta absorb an impurity hydrogen (the source of which can be materials of high-pressure cell surrounded the sample during synthesis) to form $TiH_{1.94}$, ZrH_2, or Ta_2H [7] thus preventing harmful (for j_c) MgH_2 impurity phase from appearing and hydrogen from being introduced into the material structure. Besides, it has been observed that the presence, for example, of Ti or Ta promotes the formation of MgB_{12} inclusions [8], which positively affect pinning in MgB_2-based materials [9], while the appearance of ZrB_2 in the structure does not affect the j_c of high-pressure-synthesized (HPS) MgB_2-based ceramics.

We cannot detect MgB_{12} by X-ray. It was shown [10] that MgB_{12} reflexes can be absent in the X-ray pattern due to weak diffraction signals because of a low X-ray atomic scattering factor of boron. Besides, MgB_{12} inclusions are dispersed in MgB_2, the etalon X-ray pattern of MgB_{12} is absent in the database and the literature data are contradictive.

The analysis of the oxygen distribution in the materials synthesized and sintered at 2 GPa in the temperature range from 800 to 1000°C shows that magnesium diboride matrix with near-MgB_2 stoichiometry contains about 3.5–14 % oxygen and the black inclusions with stoichiometry close to MgB_{12} contains practically no oxygen (0 - 1.5%). The correlations have not been found between the amount of oxygen in the starting B or MgB_2 and its amount in the materials produced as well as between the oxygen content and j_c [9].

According to the latest conceptions, the pinning centers in MgB_2 can be nanosized inclusions of, for example, C, SiC, etc. as well as $MgB_{2-x}O_x$ precipitates in MgB_2 matrix with diameters larger than ~ 10 nm. [11].

In the present paper we consider structural inhomogeneities of high pressure synthesized magnesium diboride-based superconducting materials without and with additions of Ti, Ta and SiC in connection with their superconducting characteristics. Special attention has been given to the synthesis and characterization of phase with near-MgB_{12} stoichiometry, which with high probability can be superconducting, and whose appearance (in the form of separate grains) in the structure of MgB_2-based materials leads to an increase of the critical current density.

Experimental

Magnesium diboride samples were high-pressure (2 GPa) and high-temperature (600 – 1050 °C) synthesized from Mg and B in recessed-anvil high-pressure apparatuses [1]. The samples were in contact with a compacted hexagonal BN powder to be protected from the contact with a graphite heater.

The initial powders of magnesium diboride contained from 0.8 to 3.5 % oxygen and of amorphous boron from 0.66 to 3.5% oxygen with grain sizes from 0.8 to 10 μm (in any particular case the detailed information about initial boron or magnesium diboride will be given). Metal magnesium chips (Technical Specifications of Ukraine 48-10-93-88) and amorphous boron were taken in the stoichiometric ratio of MgB_2. To study the influence of Ti, Ta, SiC, Ti (of size 1-3 μm, MaTecK, 99% purity), Ta (technical specifications 95-318-75, an average particle size of 1-3 μm), or SiC (200-800 nm, H.C. Starck), powders were added to the stoichiometric MgB_2 mixture of Mg and B in amounts of 10 wt%. The components were mixed and milled in a high-speed activator with steel balls for 1-3 min. The resulting powder has been compacted into tablets. The X-ray study of the initial Mg, Ti, Ta, SiC, and B has shown that the materials contained no impurity phases with hydrogen (the method accuracy being about 3-5%).

The structure of materials was studied using SEM and X-ray diffraction analyses. A scanning electron microscope ZEISS EVO 50XVP (resolution of 2 nm at 30 kV.), equipped with the

following analyzers: (1) the energy-dispersion analyzer of X-ray spectrums INCA 450 (OXFORD, England), using which the quantitative analysis from boron to uranium with a sensitivity of 0,1 wt % can be performed; (2) the detector of backscattering electrons HKL Canell 5 (OXFORD, England), which allows us to get (using the Kikuchi method) the diffraction reflections of electrons from 10-1000 nm arias and layers was employed. The critical current density (j_c) was estimated from magnetization hysteresis loops obtained on an Oxford Instruments 3001 vibrating sample magnetometer (VSM) using Bean's model. Hardness was measured employing a Matsuzawa Mod. MXT-70 microhardness tester, H_V (using a Vickers indenter) and Nano-Indenter II, H_B (using a Berkovich indenter).

Results and discussion

Studies of MgB_2 high-pressure synthesis and sintering from different initial types of amorphous boron or previously prepared MgB_2 powders (at least 8 types of B and 7 types of MgB_2 were studied) allow us to obtain nanostructural materials with 15–37 nm average grain sizes (as from X-ray patterns) and to conclude that critical currents of MgB_2-based materials are very sensitive to the quality of initial B-containing powders. The problem is that it is very difficult to analyze not only the structures of MgB_2-based materials, but the initial boron or B-containing powders as well. Each type of boron has its own "handwriting" and we cannot predict without careful study what sintering temperature will be optimal even if the pressure and time are unchanged. Optimal temperatures can vary over the wide range (600-1100°C) and for high j_c in high and low magnetic fields (in the 10-35 K interval) the optimal temperatures may be essentially different even for the same type of boron (Figures 1b, 2j). In many cases high synthesis temperatures (1050°C) bring about higher j_c in low magnetic fields and lower temperatures (800°C) in higher magnetic fields, but it is not so for all types of boron.

The highest j_c in low magnetic fields in high-pressure-synthesized (HPS) MgB_2 –based material without additions was exhibit by the samples prepared from amorphous boron B (I) at 2 GPa, 1050 °C for 1 h (Figure 1a, B (I) contained 1.66 % O and <5 μm grains, H.C. Starck). The highest *jc* at 20K in high magnetic fields (4.5–10 T) was obtained in the material high-pressure-synthesized (HPS) at 600 °C from amorphous boron B(II) and magnesium (prepared in HyperTeck, Columbus, USA), Figure 1 a. This last material in 6–10 T fields has j_c even higher than that with SiC addition (10%) prepared from B(I) at 1050°C, 2 GPa, 1 h (Figure 1 c), which is considered to be one of the best.

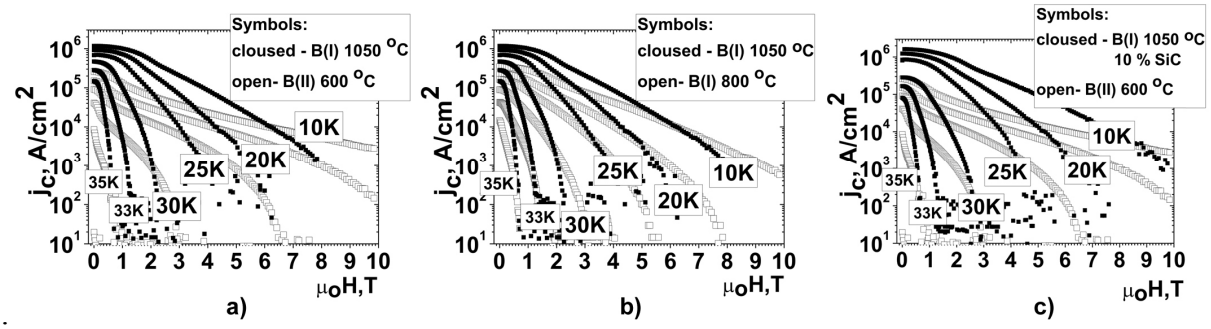

Figure 1. Dependences of critical current density, j_c, on magnetic fields, $\mu_o H$ of the samples synthesized at 2 GPa for 1 h from Mg and B, taken in the MgB_2 ratio: (a) at 1050 °C from B(I) – closed symbols and at 600 °C from B(II) – opened symbols; (b) from B(I) at 1050 °C–closed symbols and 800 °C –opened symbols; (c) at 600 °C from B(II) – opened symbols and at 1050 °C from B(I) with SiC (10 wt%)–closed symbols.

Boron B(I) contained 1.66 % O and <5 μm grains, H.C. Starck

Boron B(II) was produced by HyperTec, Columbus, Ohio, USA

Figures 2 a-h show the structures of the materials HPS from magnesium and different boron taken in MgB_2 stoichiometry at 800 and 1050°C without and with Ti, Ta, and SiC additions. The matrix of all samples contained Mg and B in near-MgB_2 stoichiometry and some oxygen (5-10 %), because of this it was marked as Mg-B-O. Structural observations show that at a synthesis temperature of about 800°C oxygen is comparatively homogeneously distributed in the material matrix (Figure 1 a), but as the synthesis temperature increases, the distribution of oxygen in the matrix is less homogeneous: the oxygen-enriched (as compared to the amount of oxygen in the matrix) areas form (Figure 1 b) and with addition of Ta or Ti such areas are transformed into separate Mg-B-O inclusions (light or white inclusions in Figures 2 d-f). All materials contain also black inclusions with near-MgB_{12} stoichiometry, the amount of which decreases with increasing synthesis temperature, and increases with Ta or Ti additions. In our opinion both MgB_{12} and Mg-B-O inclusions can positively affect pinning in MgB_2. It was shown in our previous study that after HP-synthesis Ta and Ti in many cases (especially when j_c increased) transformed into hydrides Ta_2H or Ti $H_{1,924}$ [7] and never into oxides, despite the lower enthalpy of titanium oxides formation as compared to that of titanium hydride, for example. But up to now we do not fully understand the mechanism of Ti (compare Figures 2j and 2k) or Ta influence on j_c increase in MgB_2-based materials. We can assume that the existence of the two so-called optimal temperatures for the same starting boron may be the result of competition between higher borides (MgB_{12}) formation and oxygen segregation to form Mg-B-O inclusions. Studying oxygen content we found that gray matrix of material HPS at 800°C with 10 % of Ti contained 8 % of oxygen, while gray matrix (between bright oxygen-enriched inclusions) of the materials HPS from the same boron and Mg at 1050 °C with addition of 10% Ti or Ta contained only 5 or 6 % oxygen, respectively. So, Ti and Ta seem to promote the decrease of oxygen amount in the material matrix, thus contributing to the formation of Mg-B-O inclusions with high oxygen content and pinning increase.

In the case with SiC adding inclusions of SiC by themselves as well as Mg-B-O inclusions (Figures 2j, k) can improve pinning and increase j_c (compare Figures 1b, 1c, and 2f). We succeeded in increasing j_c of MgB_2 at 10-25 K by adding 200-800 nm SiC and got highest j_c using B(I) in low and middle magnetic fields $>10^6$ A/cm^2 up to 2 and 1 T and $>10^5$ A/cm^2 up to 5 and 3.5 T at 10 and 20 K, respectively. It should be mentioned that when we add SiC of 20-30 nm and 200-400 nm SiC in HPS MgB_2-based structure Mg_2Si was formed: the higher was the amount of Mg_2Si the lower was j_c [12], especially at 25-35 K (that can be due to carbon penetration into MgB_2 lattice promoting a T_c decrease). The reactivity of SiC with coarser grains seemed to be lower and no notable interaction of SiC and MgB_2 (Figure 2 i) was observed.

The careful study of elements distribution by SEM (Figure 3 a-d) of MgB_2-based sample shown as well in Figure 2e confirmed our previous argumentation.

Unfortunately, not for each type of boron the critical current density can be increased by Ti, Ta, or SiC alloying; in many cases j_c decreases or stays unchanged.

The series of experiments on HP-synthesis of higher boride phases (MgB_4, MgB_7 or MgB_8, MgB_{12}, MgB_{16}, MgB_{17} or MgB_{20}) from Mg and B (IV) taken in 1:4, 1:6, 1:7, 1:8, 1:10, 1:12, 1:20 ratios were performed at 2 or 4 GPa, 800 or 1200 °C for 1 h. All synthesized materials were multiphased and superconducting. The highest j_c was observed for the materials synthesized from 1:8 (Figures 3 e-g) and 1:20 mixtures, whose matrix was of near-MgB_{12} stoichiometry. Reflexes in the X-ray pattern marked by "3" belong to the unidentified phase, while marked by "1" coincide with reflexes of MgB_2. Reflexes "2" without doubts can be attributed to MgO. The reflex at $2\Theta=27^o$ coincides with that of hexagonal BN, in which we wrapped samples in order to prevent them from contacting the graphite heater. A careful study of many samples allows us to conclude that this reflex belongs to higher borides (nitrogen is absent in the materials) and increases not only with increasing amount of MgB_{12}, but also when other higher-boron-containing magnezium borides (with near-MgB_{16} stoichiometry, for example) are formed. The study of T_c (inset in Figure 2g) confirmed the high amount of superconducting phase in the samples. So, there are a lot of evidences of superconductivity of MgB_{12}, but there is a very low probability of the existence of thin MgB_2

layers around the nanograins of higher borides. Because of this, we prefer not to make any final conclusion concerning the superconductivity of MgB_{12} before the results of TEM. Mechanical properties of samples with near-MgB_{12} stoichiometry differ from those with MgB_2: their Vickers microhardness (H_V) was twice as high as that of MgB_2 (25±1.1 GPa and 12.1±0.8 GPa, respectively, at a load of 4.9 N).

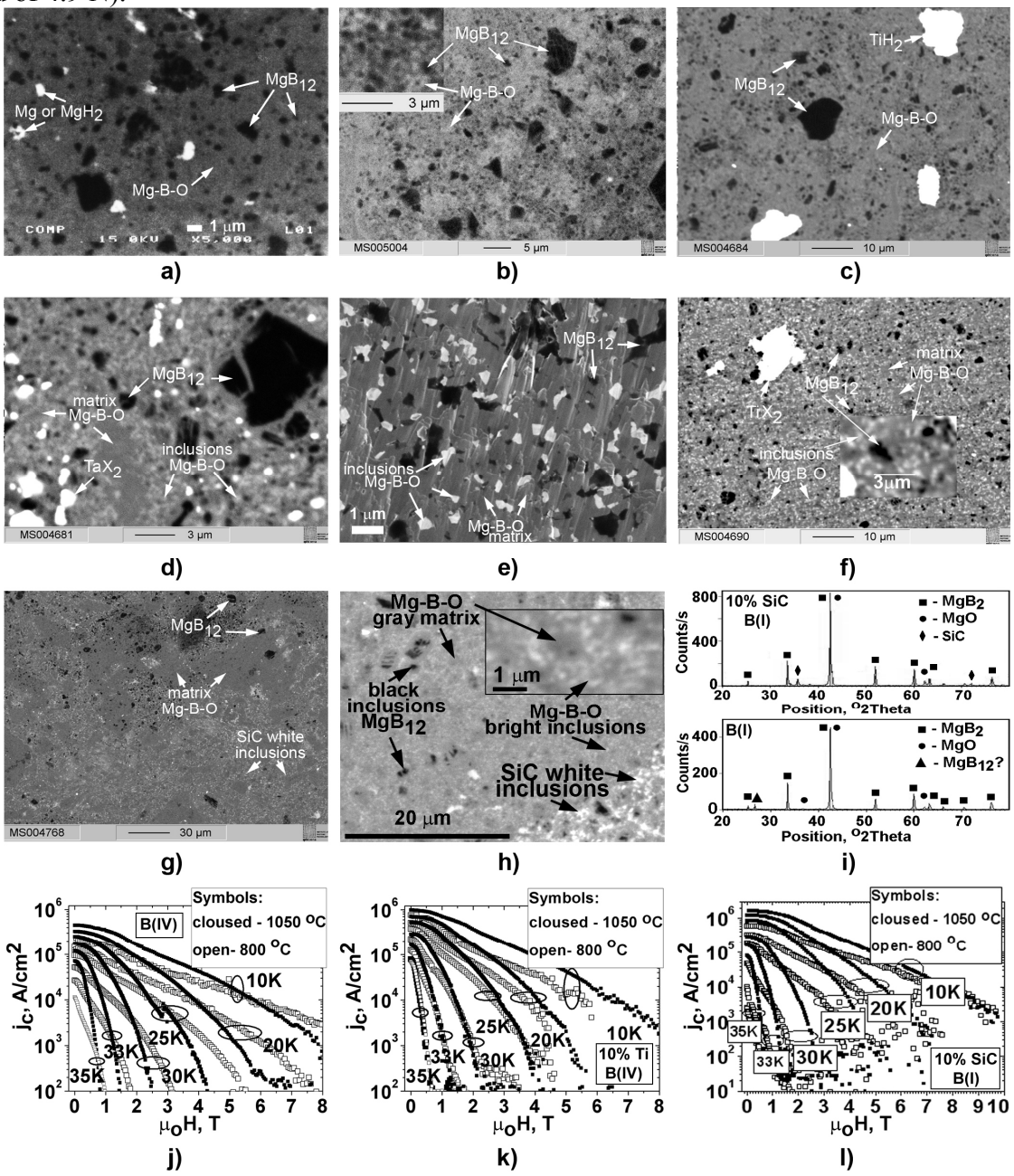

Figure 2. (a-h) Composition images (backscattering electron images) of HPS MgB_2-based materials synthesized from Mg and B taken in MgB_2 stoichiometry at 2 GPa for 1 h: (a) at 800°C from boron B(III); (b) at 1050°C from boron B(IV) (c) at 800°C with 10% Ti from boron B(IV), (d) at 1050°C with 10% Ta from boron B(IV), (e, f) at 1050°C with 10% Ti from boron B(IV) under different magnification (Fig. 2e shows the enlarged area containing no Ti , the "steers" seen in matrix are because of etching), (g, h) at 1050°C with 10% SiC from boron B(I) under different magnification (Fig. 2 h shows the enlarged area containing small amount of SiC);

(i) X-ray patterns of MgB_2 synthesized from boron B(I) with 10% SiC (upper pattern) and without;

(j-l) Dependences of critical current density, j_c, on magnetic fields, $\mu_0 H$ of the samples synthesized at 2 GPa for 1 h from Mg and B, taken in the MgB_2 ratio: (j) from B(IV) at 1050 °C–

closed symbols and 800°C –opened symbols; (k) from B(IV) with 10 % Ti at 1050°C–closed symbols and 800°C –opened symbols; (l) from B(I) with 10 % SiC at 1050°C–closed symbols and 800°C –opened symbols.

Boron B(I): 1.66 % O and <5 μm grains, H.C. Starck; boron III: 1 μm, 95–97% purity, MaTecK; boron B(IV): contained 1.5 % O, 4-μm grains, H.C. Starck

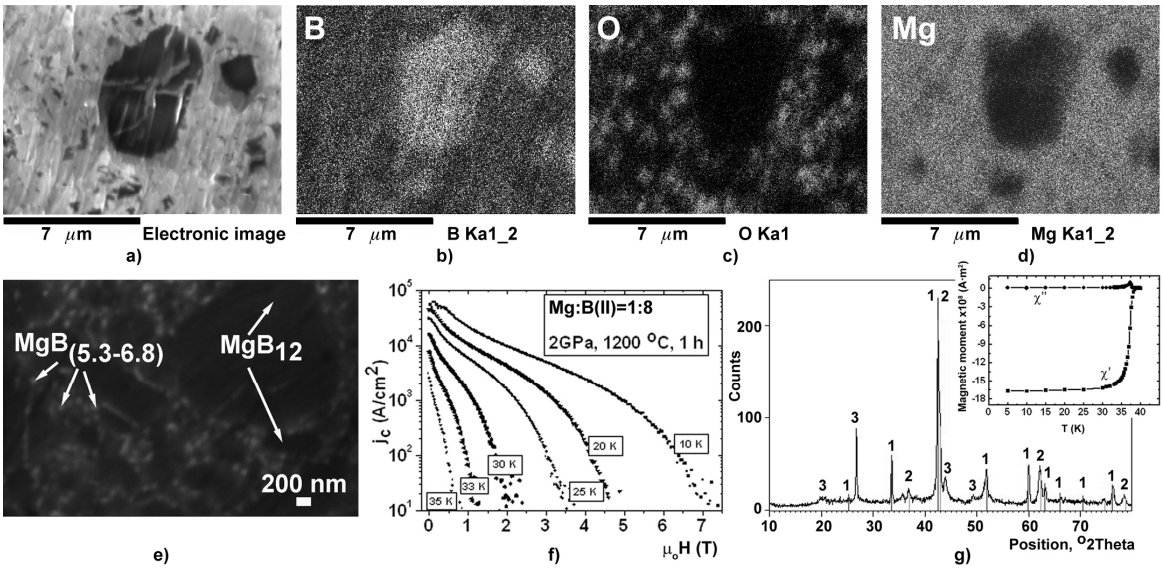

Figure 3. (a-d) backscattering electron image and analysis of elements distribution (brighter looks area higher is amount of the studied element) over the area of HPS MgB_2-based sample from Mg and B(VI) with 10% of Ti taken in MgB_2 stoichiometry at 2 GPa, 1050 °C, for 1 h: (a) electron image, (b -d) distribution of boron, oxygen and magnesium, respectively.

Conclusions

As the synthesis temperature increases from 800 to 1050°C, Ti, Ta, and SiC additions may affect the oxygen segregation and formation of Mg-B-O inclusions enriched with oxygen as compared to the amount of oxygen in the MgB_2 matrix, which can also promote an increase in pinning. Materials high-pressure synthesized from Mg and B taken in 1:4, 1:6, 1:7, 1:8, 1:10, 1:12, 1:20 ratios were superconductive with T_c of about 37 K. High j_c ($7 \cdot 10^4$-$2 \cdot 10^4$ A/cm^2 in zero field at 10 - 30 K, respectively) showed materials with the matrix composition of near-MgB_{12} stoichiometry, they have doubled microhardness of MgB_2. The final conclusion concerning possible superconducting properties of MgB_{12} will be made after the TEM study.

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