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Improvements in the MgB_2 Ceramics Formation by using a Dry Mechanical Milling Method

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Abstract:

The development of the MgB_2 manufacturing process to increase current density is an important issue to study. In this work, the MgB_2 ceramics were manufactured by using the solid-state technique. To study the influence of dry milling on the formation of the MgB_2 ceramics and grain size, variations in ball to powder weight ratio (BPR) and sintering temperature were used as control parameters. Magnesium and boron powder with stoichiometric ratio 2:1 was weighed and milled for 2 h. The milled powder was compacted and sintered at 1023 K and 1123 K for 2 h. By XRD and SEM analysis, we confirmed that the BPR ratio increased magnesium reactivity in MgB_2 ceramics formation and refined the grain size. The MgB_2 phase of 88.21% was obtained in the sample sintered at temperature of 1123 K and BPR=2:1. To determine the critical temperature of MgB_2, we select the sample with the smallest impurities phase to measure its electrical property. The critical onset temperature (Tc-onset) for the selected sample is 40.56 K (ΔTc = 0.4 K).

Keywords*: MgB_2; Milling; Solid-state; Grain size; Electrical property.*

1. Introduction

Currently, medical technology is developing quite rapidly. Magnetic Resonance Imaging (MRI) is a medical device that uses a large magnetic field to scan the internal organs of the human body. One of the sources of magnetic fields used in MRI is the niobium-based superconducting materials (NbTi or Nb_3Sn). This Nb-based superconductor has several disadvantages, including expensive raw material and low critical temperature values. Consequently, various efforts are inevitable to find alternative superconducting materials to respond these issues. In 2001, Prof. Akimitsu and his team reported that the MgB_2 material discovered in the 50's has superconducting phenomena with a critical temperature of ~40 K [1]. This critical temperature is twice as high as the critical temperature of superconducting niobium materials. In addition to the critical temperature, MgB_2 uses raw materials that are cheap and easy to synthesize. Thus, MgB_2 has the potential candidate to substitute Nb-based superconductors.

MgB_2 must be produced as a wire to be applied as a magnetic field source. MgB_2 wire fabrication can be carried out both in-situ and ex-situ. The performance of a superconducting

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wire can be indicated by its current density. Previous studies have been performed to increase the current density of the superconducting wire, include: chemical elements doping, grain refining and synthesis method [2-5]. Carbon doping (include CNT's [6], graphene [7,8], graphite [9], and nano-carbon [6]) into boron sites has been shown to increase the current density of MgB_2-based superconductors. The finer grains lead to an increase in grain boundaries, thereby strengthening the flux pinning force. Mechanical milling has been proven to refine the grain. Kurama, et al., have synthesized MgB_2 through the solid-state techniques with several process variables, including BPR, ball size, milling time, and annealing process [10]. Xu, et al., conducted a study on the effect of milling media on the superconducting properties of MgB_2. They reported that milling with toluene media produced small grain compared to ethanol and acetone [8]. Furthermore, the MgB_2 processed by milling under toluene has a higher current density value than the pure MgB_2 at 5T and 8T [8]. Based on existing methods, a dry milling method is a prospective choice. In addition to being environmentally friendly, it also promises a simpler route because it does not require a further drying process like the wet milling route.

In this work, we present the perspective of a dry mill method in air media to manufacture MgB_2 ceramics. We also explained the relationship between the ball-to powder weight ratio (BPR) and sintering temperature on the reactivity of magnesium in phase formation and the grain size of MgB_2 ceramics.

2. Materials and Experimental Procedures

For the manufacture of MgB_2 ceramics, we apply a solid-state reaction technique. The Mg powder (purity 98.5 %, particle size ≤ 0.3 mm) and powder B (95% purity, particle size 2 μm) were used in this work. With a stoichiometric ratio of Mg: B = 1:2, the precursors were weighed and milled with a shaker mill for 2 h. The influence of the BPR ratio (2:1 and 6:1) on the formation of the MgB_2 phase and its microstructure was investigated. The ball used in the milling process is a steel ball with a diameter of 5 mm. The milled powder is then poured in stainless steel (SS) tube and compacted to prevent magnesium oxidation. The encapsulated milled powder was then sintered at 1023 K and 1123 K for 2 h. All the preparation and sintering processes were performed in free-air atmosphere and naturally cooling. The sample codes are detailed in Table I.

Tab. I MgB_2 ceramics sample code.

Sample code	BPR	Sintering temperature [K]	Sintering time [h]
MB2-75	2:1	1023	2
MB2-85	2:1	1123	2
MB6-75	6:1	1023	2
MB6-85	6:1	1123	2

After sintering, the bulk sample was evacuated from the SS tube mechanically for further characterization. Bulk samples were ground with agate mortar for phase identification by an X-ray diffractometer (XRD). Rigaku SmartLab XRD with Cu Kα radiation source (λ=0.15406 nm), scan speed 5°/min, and step size 0.01 performed in the range 20-80°. A qualitative analysis of XRD patterns was carried out using Match! Software version 3 equipped with Crystallography Open Database (COD) reference database. The phase composition and lattice constants were carried out through Rietveld analysis using the General Structure Analysis System (GSAS) software [11]. The microstructure of the fracture surface of the specimen was analyzed employing a scanning electron microscope (SEM JSM-6390LA). The electrical resistivity measurement of the sample was done by the Cryogenic

Magnetometer (Oxford Teslatron) with the four-point probe (FPP) technique. The critical onset temperature (Tc-onset) and critical offset temperature (T_c-offset) was determined by taking the temperature when the resistivity value drops drastically to zero.

3. Results and Discussion

Fig. 1 shows the powder X-ray diffraction (PXRD) patterns for the four MgB_2-based samples. All sample series consists of samples with BPR=2:1 and BPR=6:1. Two sample series with BPR=2:1, sintered at 1023 K and 1123 K, were then coded MB2-75 and MB2-85, respectively. Meanwhile, the next two samples with BPR=6:1, sintered at 1023 K and 1123 K, were coded MB6-75 and MB6-85, respectively. The qualitative analysis of XRD patterns has been carried out using the Match! Software (licensed to the Center for Metallurgical and Materials Research LIPI). The four sample diffraction patterns show that the MgB_2 phase is the major phase. The indexed peaks belonging to the MgB_2 phase corresponds to COD number #100-0027 with a hexagonal crystal system and a p6/mmm space group. The appearance of the Mg phase in the MB2-75 sample indicates that Mg has not completely reacted with boron to produce MgB_2. According to several previous studies, Mg began to disappear at temperatures above 1023 K [12,13]. In addition to temperature, the reactivity of Mg was influenced by the size of magnesium and boron particles [14,15]. B_2O, Fe_2B, and MgO as a minor phase were also detected in the samples. The Fe_2B phase formation was promoted by the reaction of the steel ball to the precursor during the milling and sintering processes [13,16]. The B_2O phase that appears in the sample is the impurity phase of the raw material. The peak of the Mg phase disappears as the temperature increases, as shown in the diffraction pattern of the MB2-85 sample (Fig. 1). This is consistent with our previous study, which indicated that the formation of the MgB_2 single-phase taken place at temperatures above 1123 K [13]. The presence of the MgO phase at an angle of $2\theta = 62.15°$ was due to the influence of air during preparation.

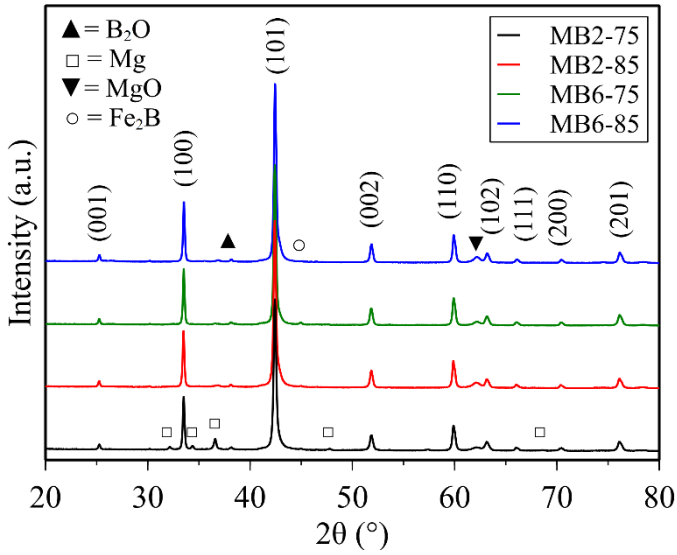

Fig. 1. Powder XRD patterns of MgB_2-based samples.

The diffraction pattern for the MB6-75 and MB6-85 samples in Fig. 1 shows that most of the peaks belong to the MgB_2 phase. The absence of the Mg phase in the MB6-75 sample indicates that the larger BPR has increased the reactivity of Mg to form the MgB_2

phase. Varghese, et al., and Aksu reported that the Mg phase began to disappear when the sintering process was performed at temperatures above 1073 K [12,17]. The sintering process at a temperature of 1023 K, which produces MgB_2 single-phase, is crucial because it inhibits further grain growth at higher temperatures. So, the dry milling method can be used as a reference to produce MgB_2-based superconducting wires.

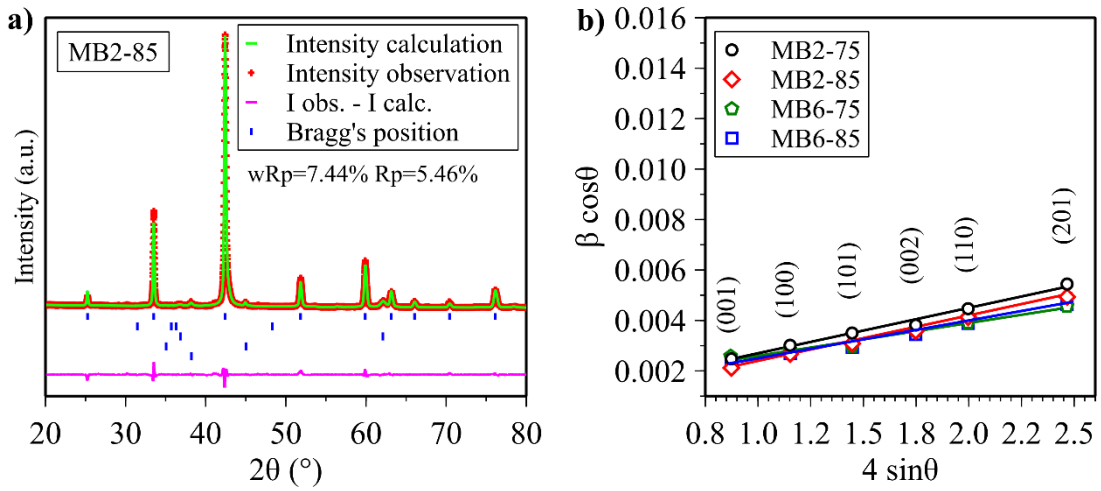

Fig. 2. a) Rietveld refinement of XRD patterns for MB2-85 sample,
b) Williamson-Hall plot of MgB_2-based samples.

Tab. II Phase quantity, lattice constants, and mean crystallite size of MgB_2 ceramics.

Sample	MgB_2 phase [wt.%]	Impurity phases [wt.%]	*a*-lattice constants [nm]	*c*-lattice constants [nm]	c/a	D [nm]
MB2-75	78.16	21.84	0.3085	0.3523	1.142	154
MB2-85	88.21	11.79	0.3085	0.3525	1.142	231
MB6-75	80.99	19.01	0.3085	0.3523	1.142	106
MB6-85	83.04	16.96	0.3085	0.3524	1.142	138

A quantitative analysis of the XRD pattern has been done by refine the pattern using the Rietveld method. The MgB_2, MgO, B_2O, and Fe_2B phases resulting from the qualitative analysis were used to estimate the phase composition. The pattern fittings have been carried out using space groups P6/mmm for the MgB_2 phase, Fm-3m (MgO phase), P-3m1 (B_2O phase), and I 4/mcm (Fe_2B phase). The resulting curves of refinement were shown in Fig. 2a. Based on the calculation, the highest MgB_2 phase weight fraction was obtained in the MgB_2 sample prepared with BPR 6:1 with a sintering temperature of 1123 K. The lattice constants for the MgB_2 phase were a=0.3085 nm and c=0.3525 nm. These results have similarities with previous reports [1,4,13,18]. The phase composition and the lattice constants of the refinement results are presented in Table II.

The results of fitting the diffraction pattern are then used to calculate the mean crystallite size of the MgB_2-based samples. The mean crystallite size was estimated using the Williamson-Hall analysis formulated as: $\beta.\cos\theta=k\lambda/D+4\varepsilon.\sin\theta$, where β is the corrected value of full width at half maximum (FWHM), $\beta=(\beta_{observation}^2-\beta_{instrumental}^2)^{1/2}$ (radians), θ is the angle of the phase peak position (°), k is the Scherrer constant (0.9), λ is the wavelength of radiation source (Cu=0.15406 nm), D is the average crystallite size (nm), and ε is micro-strain (%) [19]. In this calculation, the peaks broadening of the samples due to instrumentation factors were corrected using Al_2O_3 ($\beta_{instrumental}$ value = 0.0017 radian). Fig. 2b shows the plot of the

Williamson-Hall analysis of the MgB_2-based samples. The mean crystallite sizes of the MB2-75, MB2-85, MB6-75, and MB6-85 samples calculated by Williamson-Hall analysis were 154 nm, 231 nm, 106 nm, and 138 nm, respectively. These results show that increasing the BPR ratio can refine the crystallite size. The mean crystallite size of the MgB_2-based samples was tabulated in Table II.

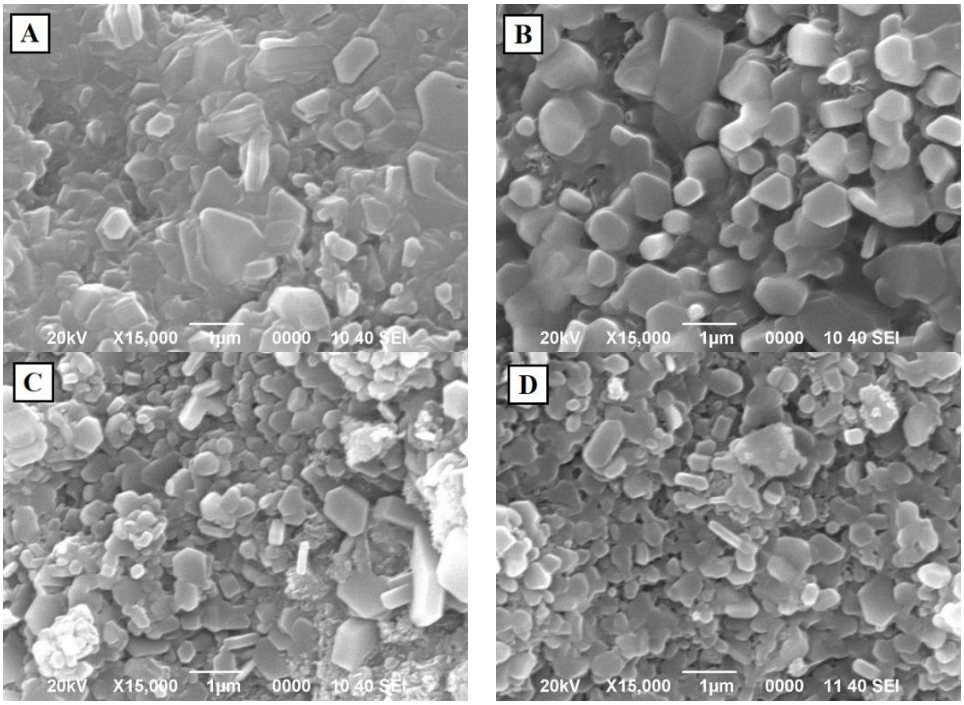

Fig. 3. Fracture surface of MgB_2 ceramics: a) MB2-75 sample, b) MB2-85 sample, c) MB6-75, and d) MB6-85.

Fig. 3 (a-d) is the secondary electron image (SEI) microstructure of the MgB_2-based samples. The dense microstructure with a polygonal shape is shown in Fig. 3a (MB2-75). Good grain interconnection is due to the existence of the Mg phase that fills the grain boundaries. The Mg phase was confirmed from the diffraction pattern in Fig. 1. As the sintering temperature raised from 1023 K to 1123 K, the polygonal microstructure with uniform direction became more pronounced. The decreasing density of the MB2-85 sample (Fig. 3b) compared to that of the MB2-75 sample was promoted by the further diffusion of magnesium to form the MgB_2 phase. Magnesium in the molten state at high temperature has played a role in increasing the porosity of the MB2-85 sample. The higher sintering temperature also has an impact on the larger grain size of the MgB2-based samples [20]. Meanwhile, samples MB6-75 and MB6-85 (Fig. 3c-d) showed the polygonal microstructure with random directions, high density, and small grain size. This result corresponds to the decrease in the mean crystallite size reported in Table II. The grain refinement of these two samples is induced by a higher BPR than the previous two samples. This MgB_2-based sample with small grain size is essential because it can increase the flux pinning. Furthermore, the increasing flux pinning can increase the value of the current density of the MgB_2-based superconductor.

The resistivity test was carried out to determine the superconducting properties of the synthesized sample. The resistivity test was performed on the selected sample (MB2-85) based on the highest MgB_2 phase weight fraction, as shown in Table II. Fig. 4 shows the temperature dependence of the resistivity curve of the MB2-85 sample in the temperature

range of 20 K – 270 K without an applied magnetic field. The resistivity value of the MB2-85 sample is 123.61 μΩ.cm and 44.34 μΩ.cm at a temperature of 265 K and 45 K, respectively. The residual resistivity ratio (RRR) of the MB2-85 sample can be calculated using the equation RRR=ρ265 K/ρ45 K and the value is 2.79. The critical temperature of onset (T_c-onset) and critical temperature offset (T_c-offset) of the MB2-85 sample are 40.56 K and 40.16 K, respectively. The results of determining the critical temperature value show that the difference between T_c-onset and T_c-offset is very small (ΔT_c = 0.4 K). The small value of ΔT_c is because the superconducting phase MgB_2 is the dominant phase in the sample (as shown in Table II).

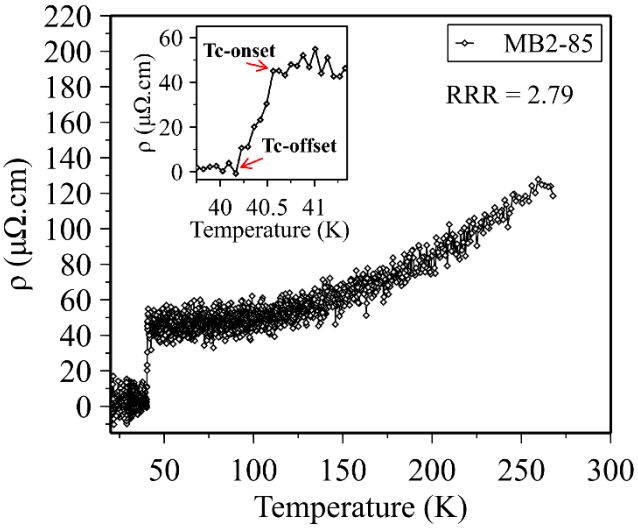

Fig. 4. Resistivity vs. Temperature curve of the selected sample (MB2-85). Inset image shows the T_c-onset and T_c-offset of the MB2-85 sample.

4. Conclusion

Manufacturing of MgB_2 ceramics by the solid-state reaction technique has been done successfully. The large BPR increases the reactivity of magnesium in the formation of the MgB_2 phase at the sintering temperature of 1023 K. Refinement of crystallite size and grain is also obtained at large BPR. The formation of the hexagonal structure of MgB_2 was promoted by raising the sintering temperature, which together causes grain growth. The highest weight fraction of the MgB_2 phase prepared by dry mechanical milling of 88.21 % is obtained at BPR 2:1 and sintering temperature of 1123 K, thus resulting in the improvement of MgB_2 phase formation. The critical onset temperature (Tc-onset) for the smallest impurities phase sample is 40.56 K (ΔT_c = 0.4 K). With these results, the mechanical milling method under air media has prospects for the manufacture of the MgB_2-based superconducting wire.

Acknowledgments

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5. References

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature, 410 (2001) 63–64.
2. H. Kurama, S. Erkus, H. Gasan, Physicochem. Probl. Miner. Process., 53, 2 (2017) 969–982.
3. F. Yang, G. Yan, Q. Y. Wang, X. M. Xiong, S. Q. Li, G. Q. Liu, J. Q. Feng, Y. C. Pang, C. S. Li, Y. Feng, P. X. Zhang, The Effect of High-energy Ball Milling on the Microstructure and Properties of Ti-doped MgB_2 Bulks and Wires, Phys. Procedia, 65 (2015) 157–160.
4. Shinya Ueda, Jun Ichi Shimoyama, Isao Iwayama, Akiyasu Yamamoto, Yukari Katsura, Shigeru Horii, Kohji Kishio, Appl. Phys. Lett., 86 (2005) 222502.
5. W Häßler, C Rodig, C Damm, J Scheiter, L Schultz, A Aubele, B Sailer, K Schlenga, Phys. C, 510 (2015) 8–12.
6. Jun Hyung Lim, Chang Min Lee, Jin Hyun Park, Jim Hyuk Choi, Jong Hyun Shim, Jinho Joo, Young Hee Lee, Won Nam Kang, Chan Joong Kim, J. Nanosci. Nanotechnol., 9 (2009) 7388–7392.
7. H. R. Liu, Z. W. Xie, L. H. Jin, F. Yang, S. N. Zhang, Q. Y. Wang, X. M. Xiong, J. Q. Feng, C. S. Li, L. Zhou, J. Mater. Sci. Mater. Electron., 31, 11 (2020) 8837–8843.
8. X. Xu, W. X. Li, Y. Zhang, K. S. B. De Silva, J. H. Kim, S. Choi, J. Nanosci. Nanotechnol., 12, 2 (2012) 1402–1405.
9. C. Shekhar, R. Giri, R. S. Tiwari, O. N. Srivastava, S. K. Malik, J. Appl. Phys., 102, 9 (2007) 093910.
10. Xun Xu, M. J. Qin, K. Konstantinov, Dayse I. Dos Santos, W. K. Yeoh, J. H. Kim, S. X. Dou, Supercond. Sci. Technol., 19, 6 (2006) 466–469.
11. A. C. Larson, R. B. Von Dreele, General Structure Analysis System (GSAS), 2004.
12. E. Aksu, J. Alloys Compd., 552 (2013) 376–381.
13. S D Yudanto, Y P Dewi, A Imaduddin, Y Nakanishi, M Yoshizawa, B Kurniawan, A Manaf, J. Supercond. Nov. Magn., 32 (2019) 2829–2835.
14. D. N. Kim, B. H. Jun, S. D. Park, C. J. Kim, H. W. Park, Prog. Supercond. Cryog., 18, 4 (2016) 9–14.
15. S. Safran, E. Kiliçarslan, A. Kiliç, A. Gencer, Cryogenics, 63 (2014) 133–137.
16. B. Jun, J. Ho, C. Kim, K. Nam, J. Alloys Compd., 650 (2015) 794–798.
17. N. Varghese, K. Vinod, A. Rao, Y. K. Kuo, U. Syamaprasad, J. Alloys Compd., 470 (2009) 63–66.
18. Sigit Dwi Yudanto, Yulia Puspa Dewi, Perdamean Sebayang, Septian Adi Chandra, Agung Imaduddin, Budhy Kurniawan, Azwar Manaf, J. Met. Mater. Miner., 30, 3 (2020) 9-14.
19. H. Shashidharagowda, S. N. Mathad, M. B. Abbigeri, Sci. Sinter., 53 (2021) 429–444.
20. D. Biswas, P. Sharma, N. S. Panwar, Sci. Sinter., 54 (2022) 201–209.

Сажетак: *Важна тема овог рада је развој производног процеса добијања MgB_2 ради повећања густине. MgB_2 керамика је добијена реакцијом у чврстој фази. Контрола параметара синтезе као што су варирање у односу куглица и праха, темшературе синтеровања је употребљена за студију утицаја млевења на формирање MgB_2 керамике и величину зрна. Прахови магнезијума и бора у стехиометријском односу 2:1 су млевени 2 сата. Млевени прахови су компактирани и синтеровани на 1023 K у 1123 K током 2 сата. XRD и SEM анализом, потврђено је да порастом односа куглица и праха расте реактивност MgB_2 керамике и рафинишу се зрна. 88.21 % фазе MgB_2 је добијено синтеровањем на 1123 K при BPR=2:1. Да би одредили критичну*

температуру MgB_2, изабран је узорак са најмање нечистоћа за електрична мерења. Критична температура (T_c-onset) за испитивани узорак је 40.56 K (ΔT_c = 0.4 K).
***Кључне речи**: MgB_2, млевење, чврсто стање, величина зрна, електрична својства.*