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# Superhard $MgB_2$ bulk material prepared by high-pressure sintering

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**Abstract**

Superhard $MgB_2$ bulk material with a golden metallic shine was synthesized by high-pressure sintering for 8 h at 5.5 GPa and different temperatures. Appropriate pressure and temperature conditions for synthesizing polycrystalline $MgB_2$ with high hardness were investigated. The samples were characterized by means of atomic force microscopy and x-ray diffraction. The Vickers hardness, bulk density, and electrical resistivity were measured at room temperature.

## 1. Introduction

The discovery [1] of 39 K superconductivity in magnesium diboride ($MgB_2$) has stimulated considerable interest in this new family of high-temperature superconductors [2–6]. In addition to superconductivity, metal borides may exhibit superhardness. However, owing to the thermal instability of $MgB_2$, the synthesis of high-density $MgB_2$ bulk material at ambient pressure is very difficult. To date, there have been few reports on the hardness of $MgB_2$. Very recently, Takano *et al* [4] reported that the Vickers hardness of $MgB_2$ bulk material is 1700–2800 kg $cm^{-2}$. In this paper, we report the preparation of high-density $MgB_2$ bulk material with much higher hardness, close to that of cubic BN. Because of its novel superconductivity and superhardness, $MgB_2$ will have significant applications in the future. Simultaneously, it will also motivate searches for new superhard materials in the metal boride series.

## 2. Experimental details

The starting material used in this work was $MgB_2$ powder that was prepared by Ren *et al* [5]. High-pressure sintering was performed in a cubic anvil high-pressure apparatus (SPD-6X1200). The starting $MgB_2$ powder was pre-pressed to make a pellet, then sealed in a Mo capsule. Figure 1 shows the sample assembly, which has fairly high stability at high pressure

  

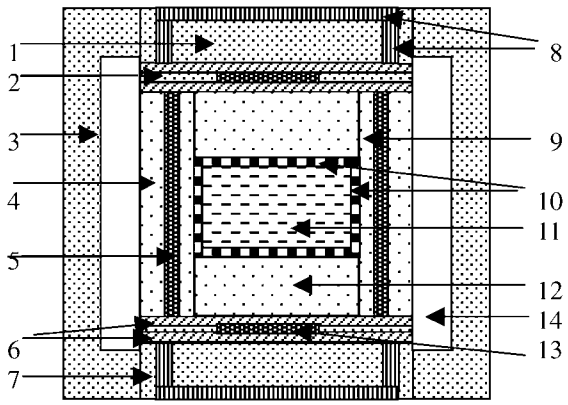


**Figure 1.** The sample assembly for the HP/HT experiment. 1, 2, 3, 7: pyrophyllite; 4: $NaCl + ZrO_2$ (20%); 5, 13: graphite heater; 6, 10: Mo; 8: steel ring; 9, 12: insulator; 11: sample; 14: dolomite.

and high temperature for a long time. While the pressure was maintained at 5.5 GPa, the heating was increasing linearly, and then a constant temperature was maintained for 8 h. Then, the samples were quenched to room temperature. Three samples were prepared at 5.5 GPa and different temperatures. Samples 1, 2, and 3 correspond to the samples sintered at 700, 800, and 1000 °C respectively. The synthesis pressure was estimated from the calibrated relation curve that was established on the basis of the phase transitions of bismuth, thallium, and barium. The synthesis temperature was determined from a relation between temperature and input power, which had been calibrated using a Pt6% Rh–Pt30% Rh thermocouple.

The samples were about 10 mm in diameter and 4 mm in height. The cross-sections of the samples were polished and observed by an optical microscope (OM) and atomic force microscope (AFM). X-ray diffraction (XRD) data were collected on a D/max-rA diffractometer using Cu K$\alpha$ radiation. A microhard tester (MHT-4) linked with an OM was used to measure the Vickers hardness of the samples. The electrical resistivity of the samples was measured using the standard four-probe technique.

## 3. Results and discussion

Observed by OM, samples 1, 2, and 3 all have golden metallic shine. The texture of sample 2 is more homogeneous than that of sample 1. Sample 3 has a darker shine than samples 1 and 2.

Figure 2 shows the AFM image of sample 2. From the AFM image, one observes that the synthesized polycrystalline $MgB_2$ consists of many microcrystallites that are micron grade in size. This reveals that at high pressure and high temperature, the starting $MgB_2$ powder recrystallizes and some microcrystallites form. The microcrystallites grow and connect with each other gradually. After high-pressure quenching, the polycrystalline $MgB_2$ forms.

The XRD patterns of the starting $MgB_2$ powder (a) and the synthesized sample 2 (b) are shown in figure 3. Comparison with the diffraction pattern for the starting $MgB_2$ powder reveals that the peak positions for synthesized sample 2 are consistent with those of the starting $MgB_2$ powder. This indicates that sample 2 has the same $AlB_2$ structure as the starting $MgB_2$ powder. In addition, we note that the relative intensity of the (101) main peak of sample 2 becomes stronger than that for the starting $MgB_2$ powder. This indicates that the orientation of sample 2 has been enhanced. Such behaviour may be attributed to the better crystallinity of sample 2 under high pressure and high temperature.

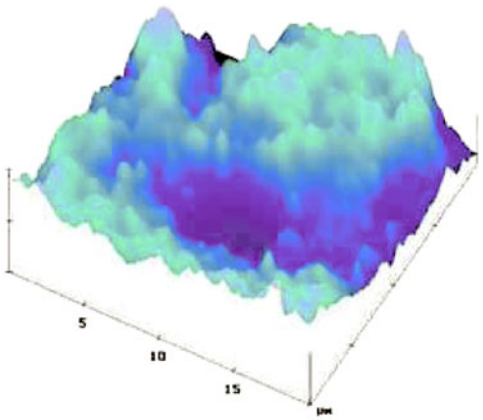


**Figure 2.** An AFM image of polycrystalline $MgB_2$ synthesized at 5.5 GPa and 800 °C.

(This figure is in colour only in the electronic version)

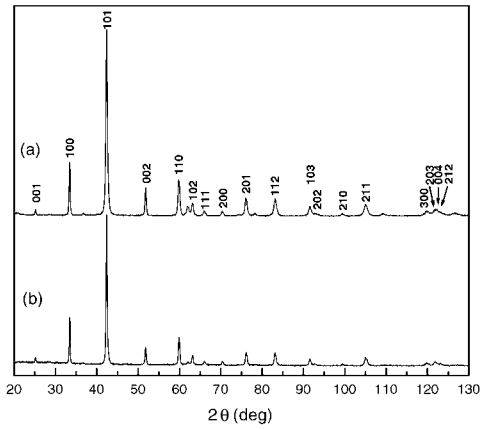


**Figure 3.** XRD patterns for (a) sample 2 and (b) the starting $MgB_2$ powder.

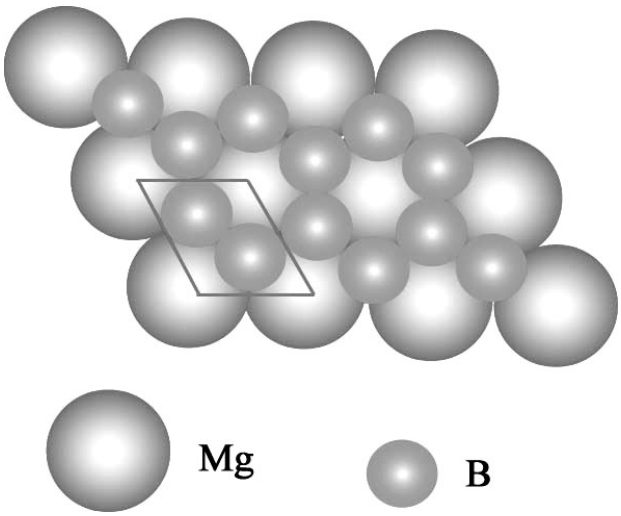


**Figure 4.** The projection of $MgB_2$ along the *c*-axis. The unit cell is marked with a rhombus.

The projection of $MgB_2$ along the *c*-axis is presented in figure 4. $MgB_2$ crystallizes in the simple structure of hexagonal $AlB_2$, which consists of alternating hexagonal layers of Mg atoms and graphite-like layers of B atoms. The XRD pattern indicates the synthesized polycrystalline bulk material to have better orientation along the *c*-axis.

Table 1 shows the Vickers hardness, bulk density, and resistivity for the samples synthesized under different conditions. It should be pointed out that the sintering temperature has a significant effect on the hardness of the samples. At 800 °C, the synthesized sample has the highest hardness (4109.5 kg $cm^{-2}$) in comparison with the other two samples which were sintered at 700 and 1000 °C; i.e. at lower and higher temperature than 800 °C, the hardness decreases sharply. This behaviour may arise from the different degrees of crystallinity of

**Table 1.** Measured data: Vickers hardness ($H_V$), bulk density ($D$), and electrical resistivity ($\rho$) for samples prepared under different synthesis conditions.

| Sample no | $H_V$ (kg cm$^{-2}$) | $D$ (g cm$^{-3}$) | $\rho$ ($10^{-6}$ Ω m) | $P$ (GPa) | $T$ (°C) |
|---|---|---|---|---|---|
| 1 | 2153.3 | 2.70 | 3.03 | 5.5 | 700 |
| 2 | 4109.5 | 2.71 | 2.42 | 5.5 | 800 |
| 3 | 1448.8 | 2.88 | 2.75 | 5.5 | 1000 |

$MgB_2$ at difference synthesis temperatures. At 800 °C, the synthesized sample has a better degree of crystallinity. However, at lower temperature (700 °C), the crystallinity of the $MgB_2$ is insufficient. At higher temperature, the sample may partially decompose from $MgB_2$ to $MgB_4$, which may be responsible for the decrease of the hardness of sample 3. It should also be noted that the synthesized samples have extremely high density.

The data on resistivity in table 1 show the metallic nature of the samples synthesized by high-pressure sintering. The three samples show resistivities at room temperature that are quite different. Sample 2 has higher resistivity than the other two samples. This is attributed to the different crystallinities of the three samples.

Finally, it should also be pointed out that the synthesized $MgB_2$ samples have better chemical stability than the starting $MgB_2$ powder. It is not easy to dissolve them in strong acid.

## 4. Conclusions

By high-pressure sintering, we have synthesized $MgB_2$ bulk material. Besides its superconductivity, it possesses many other excellent properties such as high hardness, high density, better conductivity, and high chemical stability. In particular, its Vickers hardness can be as high as 4109.5 kg cm$^{-2}$, which is close to the hardness of cubic BN. The appropriate synthesis conditions for this kind of superhard $MgB_2$ bulk material are 5.5 GPa and 800 °C in this study. Since polycrystalline $MgB_2$ has such high hardness, it is believed that single-crystal $MgB_2$ will show much higher hardness than polycrystalline $MgB_2$. These excellent properties dominate its various potential applications. At the same time, this will stimulate the search for new superhard materials among the metal borides.

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