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Influence of Mg deficiency on the properties of MgB_2

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Abstract

The samples of Mg deficiency with different Mg nominal content ($Mg_{1-x}B_2$) are prepared by the solid-state reaction method at the sintering temperatures of 900 and 640 °C. The effects of Mg deficiency on the structure and superconducting properties are investigated by the Rietveld refinement of X-ray powder diffraction and the resistance measurement, respectively. The results show that the lattice parameters of the samples sintered at different temperatures are of a similar variation, i.e., a decreasing and c increasing with increasing x, respectively. T_c of the samples decreases with increasing x and the maximum T_c variation of $\Delta T_c(T_c^{max} - T_c^{min}) \sim 2$ K is observed for samples sintered at high temperature. It is concluded that the nominal Mg content reduction does not give rise to serious Mg deficiency and slight Mg deficiency does not result in a remarkable change of T_c and normal state properties of the samples.

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Keywords: MgB_2; Deficiency; Lattice parameter

1. Introduction

Magnesium diboride is a material known since early 1950s [1]. Akimitsu's group [2] reported the superconductivity of MgB_2 on January 10, 2001 at a conference in Sendai, Japan. Then people took great interest in it because its critical temperature ~40 K is close to or above the theoretical limit predicted from the BCS theory [3]. Unlike high temperature cuprate superconductors, MgB_2 has simple crystal structure, low anisotropy, large coherence length, high critical current density, transparency of grain boundaries to current flow [4], which makes it a good candidate for large scale applications. During the last one-year, many groups fabricated samples in various forms and made much effort in researching new superconducting borides by doping or substitution at Mg or B sites. In addition, people also find that nonstoichiometry of B can remarkably influence the superconductivity of metal diborides. Such as beryllium boride, Felner et al. [5] found BeB_2 was nonsuperconducting in stoichiometric form, but Young et al. [6] found it was superconducting at 0.7 K for the composition $BeB_{2.75}$. For MgB_2 superconductors including bulk, powders, wires, tapes and thin films, they are usually prepared at the temperature highly above the melting point

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(648 °C) of Mg. It is well known that Mg is highly volatile at high temperatures. Therefore, it is inevitable that Mg is easy to loss during the preparing process of the sample. That is to say, the prepared samples usually exist Mg deficiency, in particular, for the film sample. Hence, to obtain samples with high quality, it is necessary and important to investigate the effect of Mg deficiency on the structure and superconductivity of MgB_2. So far, there are only a few investigations as to Mg deficiency problem [7,8]. In this article, the effect of Mg deficiency on the structure and superconductivity of MgB_2 is investigated in detail by changing the nominal stoichiometry of $Mg_{1-x}B_2$ samples intentionally and performing heat treatment at high and low temperatures.

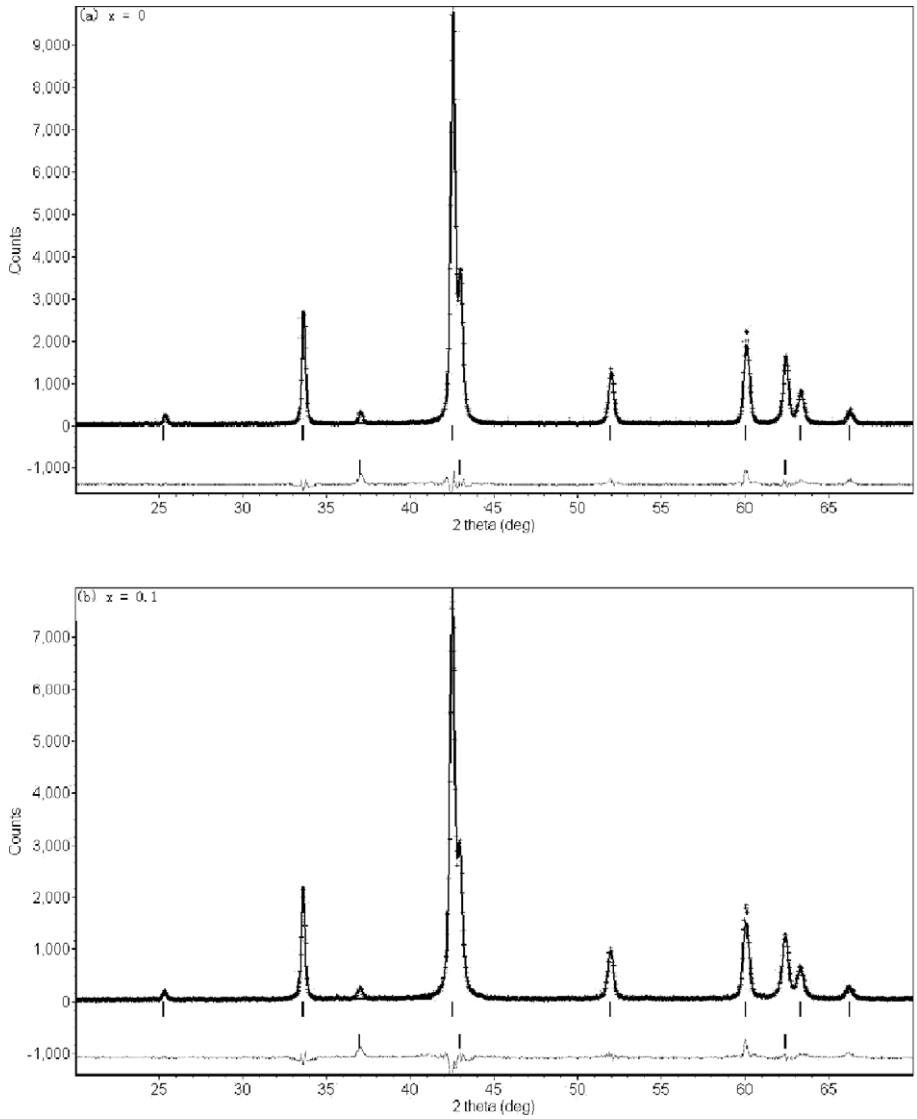

Fig. 1. XRD patterns of $Mg_{1-x}B_2$ samples sintered at $T = 900$ °C (a) $x = 0$, (b) $x = 0.1$. Crosses indicate the experimental data and the calculated profile is the continuous line overlying them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

2. Experimental

A group of $Mg_{1-x}B_2$ samples with nominal composition $x = 0$, 0.1, 0.2, 0.5 were prepared by solid-state reaction method. Mg flakes and B powder were mixed and pressed into pellets. These pellets were wrapped up in Mo foil and then placed in Mo tubes and heated under a 95%Ar:5%H_2 gas flow at 900 °C for 2 h. The samples were furnace-cooled to room temperature under the mixed atmosphere. We refer to this group of samples as group A. Another group of $Mg_{1-x}B_2$ samples with nominal composition $x = 0$, 0.3, 0.6 were prepared in the same method but sintered at 640 °C for 30 h. We refer to this group of samples as group B.

Powder X-ray diffraction (XRD) for the $Mg_{1-x}B_2$ samples was performed using a Philips PW 1700 X-ray diffractometer with Cu K_α radiation. The resistance for the $Mg_{1-x}B_2$ samples was measured as a function of temperature by the standard four-probe technique.

3. Results and discussion

For group A samples, XRD at room temperature shows the main phase is MgB_2 with a small amount of MgO and no extra diffraction peak from MgB_4 is observed. It is found that the peak positions of the MgB_2 phase change with the increase of x, which indicates that the lattice parameters change with x.

The structural parameters of the samples can be refined by the standard Rietveld technique [9]. MgB_2 phase can be indexed as hexagonal structure with space group P6/mmm and MgO phase can be indexed as cubic structure with space group Fm3m. Fig. 1(a) and (b) shows experimental and calculated XRD patterns for sample $x = 0$ and $x = 0.1$, respectively.

The relationship between lattice parameter and x is shown in Fig. 2. It is found that lattice parameter c increases approximately linear with the increase of x, while lattice parameter a decreases approximately linearly with x increasing. The calculated Mg deficiency is about 7–13%.

The temperature dependence of resistivity for the samples is shown in Fig. 3. The resistance has been normalized to the resistance of 50 K. All samples show a narrow transition width of ~0.5 K, indicating the good homogeneity of the samples. It can be seen clearly that both the onset transition temperature T_c^{onset} and zero resistance transition temperature T_{c0} decrease with the increase of x. T_c^{onset} is 40.4, 39.4, 38.4, 38.2 K for the samples with $x = 0$, 0.1, 0.2, 0.5, respectively. The difference between T_c of two samples with $x = 0$ and 0.5, $\Delta T_c(T_c^{x=0} - T_c^{x=0.5})$, is 2.2 K, which indicates that nominal Mg deficiency has little influence on T_c of the samples.

The temperature dependence of normalized resistance in the temperature range from 20 to 300 K is shown in inset of Fig. 3. The residual resistivity ratio ($RRR = R_{300\ K}/R_{42\ K}$) of samples with $x = 0$, 0.1, 0.2, 0.5 is 2.96, 2.58, 2.63, 2.07, respectively. It

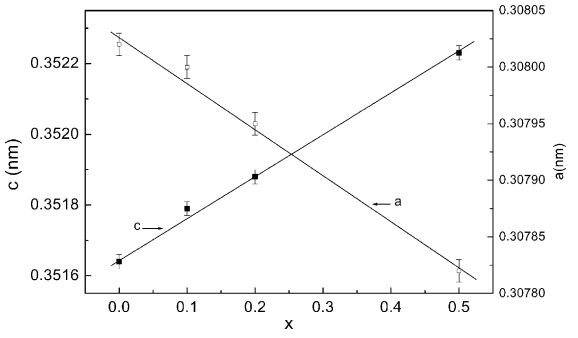

Fig. 2. The variation of the lattice parameters with x ($Mg_{1-x}B_2$ samples sintered at 900 °C).

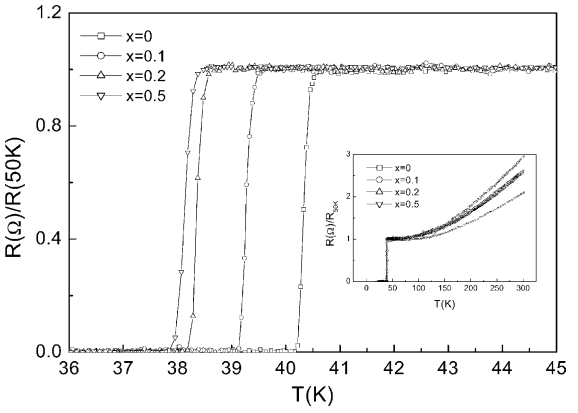

Fig. 3. The temperature dependence of resistance of $Mg_{1-x}B_2$ samples sintered at 900 °C.

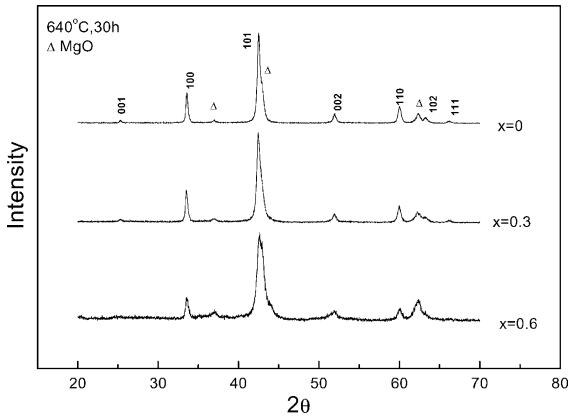

Fig. 4. XRD patterns of s $Mg_{1-x}B_2$ samples sintered at 640 °C.

is concluded that nominal Mg deficiency does not make much difference on the normal state transport properties. $\rho = \rho_0 + aT^b$ is used to fit the $R(T)/R(50\ \mathrm{K})$ curve in the temperature range from 120 to 300 K and the results show b is about 1.898–2.108, which indicates that the model of transport is e–e scattering.

For the samples of group B, their XRD patterns are shown in Fig. 4. MgB_2 and a small amount of MgO are found in the patterns. The relationship between the lattice parameter a and c of the samples and x is shown in Fig. 5, which is similar to the results of group A samples. However, the calculated Mg deficiency is about 2–5% for group B samples, obviously lower than that of group A samples. This low Mg deficiency for group B samples is attributed to its low sintering temperature of 640 °C, lower than the melting point of Mg, which results in reduction of Mg volatilization.

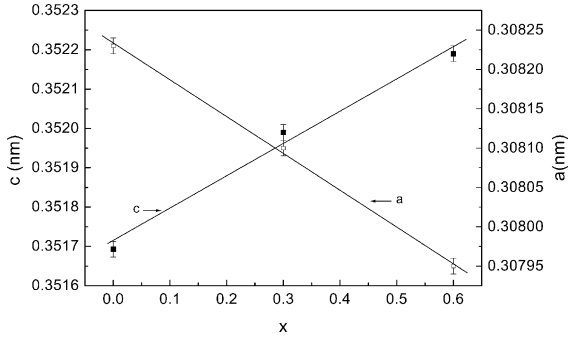

Fig. 5. The variation of the lattice parameters with x ($Mg_{1-x}B_2$ samples sintered at 640 °C).

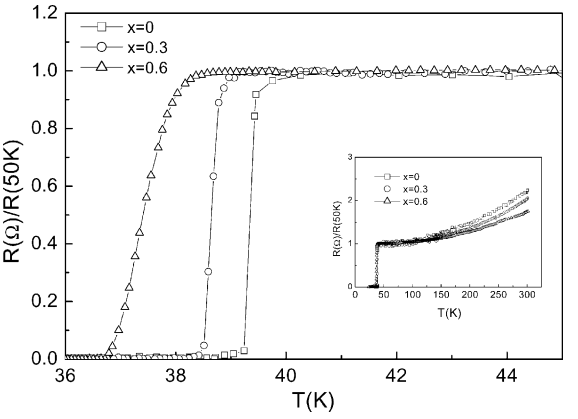

Fig. 6. The temperature dependence of resistance of $Mg_{1-x}B_2$ samples sintered at 640 °C.

The temperature dependence of normalized resistance of group B samples is shown in Fig. 6. Analogous to the group A sample, T_c of the samples also decreases with the increase of x. T_c^{onset} is 39.4, 38.7, and 37.9 K for the samples with $x = 0$, 0.3, 0.6, respectively. $\Delta T_c(T_c^{x=0} - T_c^{x=0.6}) = 1.5$ K is slightly smaller than that of samples of group A. The $R(T)/R(50\ \mathrm{K})$ curve in the temperature region from 20 to 300 K is plotted in inset of Fig. 6. The residual resistivity ratio ($RRR = R_{300\ \mathrm{K}}/R_{42\ \mathrm{K}}$) of 2.2, 2.0, 1.7 are obtained for samples $x = 0$, 0.3, 0.6, respectively, which is smaller than that of group A samples. The model of transport can be fitted by e–e scattering too and the calculated b is about 2.008–2.044.

Above results indicate that the actual Mg deficiency levels of the sample sintered at high and low temperature are all much lower than the nominal Mg deficiency level. This means that Mg has a tendency preferring to integrate with B to form MgB_2 phase. In addition, a small amount of Mg deficiency does not affect T_c and normal state property of the samples strongly, which is pronouncedly different from the effect of B deficiency [10].

4. Conclusions

The effects of Mg deficiency on the structure and superconducting properties of the $Mg_{1-x}B_2$

samples are investigated by the Rietveld refinement of XRD and the resistance measurement, respectively. The results show that lattice constant a decreasing and c increasing with increasing x, respectively. T_c of the samples decreases with increasing x and the maximum T_c variation of $\Delta T_c(T_c^{max} - T_c^{min}) \sim 2$ K is observed for samples prepared at high temperature. It is concluded that the nominal Mg content reduction does not give rise to serious Mg deficiency and slight Mg deficiency does not affect T_c and normal state properties of the samples strongly.

Acknowledgements

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