Synthesis and Electrical and Magnetic Properties of Li$_x$B$_{1+y}$C$_{1-y}$

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Abstract. We had prepared Li$_x$B$_{1+y}$C$_{1-y}$ and investigated their electrical properties in order to study the possibility of the superconductivity in Li$_x$BC. Samples were prepared by the two-step heat treatment. Firstly, Li$_x$B$_{1+y}$C$_{1-y}$ with $x \sim 1$ was prepared at 1473 K for 3 hours in Ar atmosphere from starting materials with Li:B:C=1.25:1+y:1−y. Single phase samples were obtained for $-1.05 \leq y \leq 0.20$. While the lattice parameter $a$ was almost independent of $y$, the lattice parameter $c$ showed a curious $y$ dependence. The temperature dependence of the electrical resistivity for all samples showed a semiconducting behavior. Its absolute value was not dependent on $y$. The Li deintercalation from above samples was carried out by Zr gettering at 1173 K for 150 hours in a vacuum. Li content $x$ became $\sim 0.8$. The electrical resistivity decreased with decreasing $x$. Some samples showed a metallic behavior and the superconducting-like decrease in the electrical resistivity below $\sim 20$ K.

1. Introduction

Magnesium diboride MgB$_2$ which superconducting transition temperature $T_c$ was 39 K was discovered by Nagamatsu et al. in 2001 [1]. The constituent elements of MgB$_2$ are light elements and the origin of such high-$T_c$ superconductivity is considered to be due to the high phonon frequency of light elements. Lithium borocarbide Li$_x$BC also consists of light elements and its crystal structure is very similar to that of MgB$_2$ (Fig. 1) [2]. The Li content $x$ can be changed without destructing its crystal structure. High-$T_c$ superconductivity with $T_c$ of about 100 K is theoretically predicted in hole-doped Li$_x$BC with $x = 0.5$ [3]. Although many researchers have tried to find the superconductivity in Li$_x$BC, they failed and did not obtain even metallic conduction.

Recently, Fogg et al. [4] reported that the phase separation to the B-rich phase and C-rich phase from Li$_x$BC occurred with decreasing $x$. However, they suggested that the high-$T_c$ superconductivity became possible when such phase separation due to the exchange of B and C atoms were suppressed. We have tentatively succeeded to prepare the metallic Li$_x$BC and the superconducting-like decrease in the electrical resistivity below $\sim 20$ K by the Zr gettering and the long time annealing.

Then, in this study, we report the preparation method of Li$_x$B$_{1+y}$C$_{1-y}$ and their electrical properties.
2. Experimental
Hole-doped Li$_x$B$_{1+y}$C$_{1-y}$ was prepared by the two-step heat treatment described below. Firstly, the parent Li$_x$B$_{1+y}$C$_{1-y}$ was prepared by using Li (ingot, 99 % ), B (powder, 99 % ) and C (powder, 99.9 % ) as starting materials. The composition ratio of starting materials was $x = 1.25$, $y = 0$, $±0.05$, $±0.10$, $±0.15$, 0.20. The excess amount of Li was necessary in order to prepare the parent Li$_x$BC because the Li vapor was important for the formation of Li$_x$BC structure. The B and C powders were weighed in desired ratio, mixed and pressed into pellets. Pellets and Li ingot were loaded into Ta tube in Ar atmosphere and the Ta tube was welded in Ar atmosphere. Then, Ta tube was heat treated at 773 K for 3 hours and at 1473 K for 3 hours under a flow of Ar.

After this procedure, hole-doped Li$_x$B$_{1+y}$C$_{1-y}$ was obtained from the parent Li$_x$B$_{1+y}$C$_{1-y}$ by the Li deintercalation. The parent Li$_x$B$_{1+y}$C$_{1-y}$ and Zr foils were inserted into quartz ampoules and sealed in a vacuum of about $2 \times 10^{-3}$ Pa. Quartz ampoules were heated at 1173 K for 150 hours.

The powder X-ray diffraction measurement was carried out by RIGAKU RINT 1100. Lattice parameters and Li content $x$ were determined by the Cohen’s least square method and RIETAN-2000 program [5]. The tentative determination of the Li content by ICP measurement suggested that the Li content estimated by the chemical analysis was close to that by Rietveld analysis. The electrical resistivity measurement was carried out using Quantum Design PPMS system.

3. Results and Discussion
Figure 2 shows the powder X-ray diffraction patterns of the parent and the hole-doped Li$_x$B$_{1+y}$C$_{1-y}$. All samples keep a LiBC crystal structure and any phase separations are not observed. It is different from the previous report [4]. Although small impurity phases are observed in the parent samples with $y = ±0.05$, 0.15, they disappear during the Li deintercalation. The long time annealing exclude impurity phases and may promote the ordering of B and C atoms in the BC plane. The Li contents of the parent and the hole-doped Li$_x$B$_{1+y}$C$_{1-y}$ are about 1.0 and 0.8, respectively, and almost independent of $y$. Zr foils act as a Li getter. The lattice parameters $a$ and $c$ of both Li$_x$B$_{1+y}$C$_{1-y}$ are shown in Fig. 3. Although the lattice parameter $a$ is almost independent of $y$, the lattice parameter $c$ shows a curious $y$ dependence. The origin of this behavior is not elucidated now.

The temperature dependences of the electrical resistivity are shown in Fig. 4. The absolute values of the electrical resistivity of the parent Li$_x$B$_{1+y}$C$_{1-y}$ are distributed between $10^{-3}$ and $10^4$ Ω·cm, and seem to be independent of $y$. All parent Li$_x$B$_{1+y}$C$_{1-y}$ show a semiconducting behavior (Fig. 4(a)). On the other hand, the absolute values of the electrical resistivity of hole-doped Li$_x$B$_{1+y}$C$_{1-y}$ are lower than those of the parent Li$_x$B$_{1+y}$C$_{1-y}$ (Fig. 4(b)).
absolute values are not also dependent on $y$. The decrease rate of the electrical resistivity by the Li deintercalation in the high resistive parent $\text{Li}_x\text{B}_{1+y}\text{C}_{1-y}$ is larger than that in the low resistive parent $\text{Li}_x\text{B}_{1+y}\text{C}_{1-y}$. However, the metallic $\text{Li}_x\text{B}_{1+y}\text{C}_{1-y}$ is obtained from the low resistive parent $\text{Li}_x\text{B}_{1+y}\text{C}_{1-y}$. The hole-doped $\text{Li}_x\text{B}_{1+y}\text{C}_{1-y}$ with $y = 0.15$ shows a metallic behavior and further the drastic decrease below $\sim 20$ K. The drastic decrease in the electrical resistivity resembles superconductivity.

![Figure 2. The powder X-ray diffraction patterns: (a) the parent samples and (b) the hole-doped samples.](image)

![Figure 3. The lattice parameters $a$ and $c$: (a) the parent samples and (b) the hole-doped samples.](image)
4. Conclusion

We have firstly succeeded to prepare the metallic Li$_x$BC by the two-step heat treatment. In the Li deintercalation process, the gettering by the Zr foils and the long time annealing are important to obtain the metallic Li$_x$B$_{1+y}$C$_{1-y}$. The metallic Li$_x$B$_{1+y}$C$_{1-y}$ shows the drastic decrease in resistivity like a superconductivity. In order to investigate the origin the drastic decrease below ∼ 20 K, the magnetization measurement is necessary and now in progress.

References

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