Electrochemical synthesis of superconductive MgB_2 from molten salts

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Abstract

We have found that superconductive MgB_2 can be electrochemically synthesized from molten salts. The electlysis was performed in an Ar flow at 600°C on fused mixtures composed of $MgCl_2$, MgB_2O_4, $Na_2B_2O_4$ and alkali halides such as KCl, NaCl, and LiCl. Superconductivity was observed for a wide variety of electrolytes. It was also found that the magnetic and electrical transport properties are the most improved for samples prepared from $MgCl_2$-NaCl-KCl-MgB_2O_4 electrolytes.

Key words: MgB_2; superconductivity; electrochemical synthesis; molten salts

The recent discovery of superconductivity in MgB_2 at a transition temperature (T_C) as high as 39 K [1] has aroused much attention not only in fundamental physics but also in the field of applied superconductivity [2]. Many experimental studies have shown that this high-T_C transition is plausibly brought about by the phonon-mediated BCS mechanism [2]. For the purpose of practical applications, wires, tapes, and thin films as well as bulk samples have been fabricated by means of direct reactions between elemental Mg and B, and their properties have been investigated in detail [2].

We have recently proposed a method for the electrochemical synthesis of MgB_2 [3,4]. Black deposits containing MgB_2 were obtained by means of electrolysis on fused mixtures of $MgCl_2$, KCl and MgB_2O_4 at 600°C in an Ar flow. The simple installation, moderate reaction conditions, and low-cost starting materials used in this method are favorable for industrial application. It was also found that the partial substitution of NaCl for KCl produced an improvement of electrical transport properties, which allows the transport measurements with considerable reliability [4]. The observation of a resistive transition indicates that this method of synthesis has a potential for practical fabrication of devices and magnets. The upper critical field and the coherence length evaluated from the field dependence of electrical resistivity were close to the previous values obtained for bulk samples [4].

In this paper, to optimize the synthesis condition, we have carried out the substitution of KCl by other alkali halides as well as the replacement of the borate MgB_2O_4 by $Na_2B_2O_4$, and have evaluated the superconducting properties of the samples from magnetic measurements.

The electrolysis was carried out by the same process as that reported in the previous work [3,4]. Several alkali halides, such as LiCl and NaCl, and the Na-borate $Na_2B_2O_4$ were substituted in an electrolyte consisting of $MgCl_2$, KCl, and MgB_2O_4, which had a molar ratio of 10: 10: 2. From ionic current measurements during the electrolysis, the melting points of the electrolytes were about 450°C for the substituted electrolytes but about 580°C for the non-substituted electrolyte. The magnetic properties were measured using a SQUID magnetometer with an applied field of 20 Oe. Other details have been given elsewhere [3,4].

Figure 1 shows the FC (field-cooled) and ZFC (zero-field-cooled) magnetic susceptibilities plotted as a

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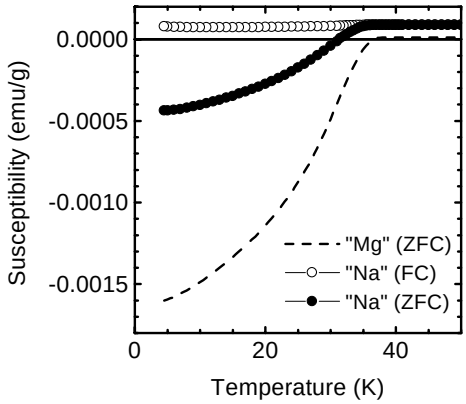

Fig. 1. Magnetic susceptibility plotted against the temperature with a field of 20 Oe for the two samples. Details are noted in the text.

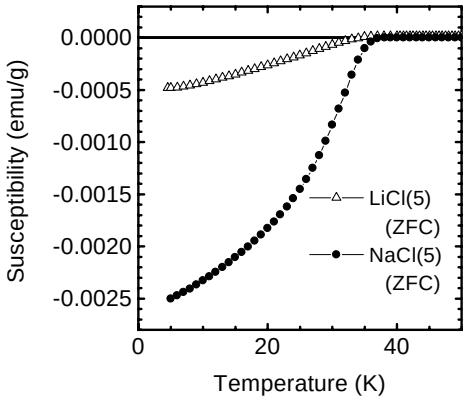

Fig. 2. ZFC magnetic susceptibility plotted against the temperature with a field of 20 Oe for the LiCl(5) and NaCl(5) samples.

function of the temperature for the two samples. The data of the sample denoted as "Mg" was taken from Ref. [3]. This sample was prepared from the electrolyte of $MgCl_2$, KCl, and MgB_2O_4 whose molar ratio is 10: 10: 2. The other sample, labeled as "Na," was prepared from the electrolyte of $MgCl_2$, KCl, and $Na_2B_2O_4$ with the same molar ratio. The latter sample exhibits similar shapes of FC and ZFC curves to those of the former sample. The diamagnetic behavior at low temperatures shows the Meissner effect of superconductivity. For both samples, the onset of the superconducting transition was seen at about T_C=37-38 K. Isothermal magnetization measurements were also conducted at 4.5 K and provided magnetic hysteresis accompanied by sharp cusps around a zero magnetic field, which is characteristic of type-II superconductors, as shown in Ref. [3].

In spite of the difference between the low-temperature susceptibilities of the samples, the presence of superconductivity for the "Na" sample means that MgB_2 is synthesized through the reaction between the Mg ion in $MgCl_2$ and the B ion in $Na_2B_2O_4$. This situation is plausibly true for the "Mg" sample as well: the MgB_2 formation originates from the reaction between Mg in $MgCl_2$ and B in MgB_2O_4 and not from the decomposition of MgB_2O_4. In fact, superconductivity has not been clearly observed for the samples prepared from the electrolytes without $MgCl_2$.

This figure also shows that the absolute values of the low-temperature ZFC susceptibilities below T_C are larger for the MgB_2O_4-based electrolyte, indicating a larger fraction of MgB_2. As was noted earlier, the electrical transport properties were improved for the substitution of NaCl for KCl in the $MgCl_2$-KCl-MgB_2O_4 electrolyte [4]. From these experimental results, we investigated the substitution effects of some alkali halides (LiF, LiCl, and NaCl) for KCl in a MgB_2O_4-based electrolyte to obtain further improvement of the magnetic properties. The contents (x) of the alkali halides (AX) were changed between 0 and 10 in the molar ratio of $MgCl_2$, AX, KCl, and MgB_2O_4, 10: x: (10-x): 2. The samples will be denoted as $AX(x)$.

One representative result is shown in Fig. 2, where the ZFC magnetic susceptibilities are plotted as a function of the temperature for the LiCl(5) and NaCl(5) samples. It can be clearly seen that the LiCl-substitutied electrolyte (LiCl(5)) leads to the superconducting transition at almost the same T_C as that shown in Fig. 1, accompanied by the diamagnetic behavior below about 35 K. However, the absolute values of the susceptibilities below T_C of this sample are much smaller than those of NaCl(5). The same qualitative trend was also observed for the other samples prepared from the electrolytes containing LiCl and LiF. So far, the largest low-temperature ZFC susceptibilities have been obtained for the NaCl-substituted electrolytes with x=3-7.

Thus, on the basis of these results, the magnetic and transport properties were the most improved for samples prepared from $MgCl_2$-NaCl-KCl-MgB_2O_4 electrolytes in the present synthesis method. Further studies, including research on the sample preparation with changing the reaction temperature, are currently in progress to obtain better conditions for synthesis. The results will be published soon.

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