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Flux Growth and Magnetic Properties of CaB_6 Crystals

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Lanthanum doped calcium hexaboride, $Ca_{1-x}La_xB_6$, attracts a lot of interest because of high temperature weak ferromagnetism though the material consists of no magnetic elements.[1)] However, there have been some doubts about this material. For example, some of the samples did not have ferromagnetism.[2)] Impurities in the samples were not examined well in spite of weak ferromagnetism. In addition, procedures of the sample preparation were not reported in detail in the reports. Therefore, we prepared single crystals of $Ca_{1-x}La_xB_6$ while paying attention to a main impurity, iron, and examined the relation between the impurity and the ferromagnetism.

Undoped and lanthanum-doped CaB_6 crystals were prepared by the flux method. The CaB_6 starting material was synthesized by reaction of $Ca(OH)_2$ and boron.[3)] Aluminium metal, Al, was of nominal purity of 4N. The CaB_6 and aluminium, 50–52 g in a total weight, were put into an AlN crucible. A molar ratio of CaB_6 to Al was 0.6%.[4)] Ca was also added as a form of $Ca(OH)_2$ into the crucible in order to suppress formation of AlB_2 crystals. The amount of Ca was 20 mol% of the CaB_6 solute. Lanthanum was doped by adding commercial LaB_6 powder.

The samples were kept at 1450°C in a flow of argon for 24 h, slowly cooled to 800°C by 15°C every hour, and then quenched. The aluminium flux was removed in NaOH solution. Magnetization of undoped calcium hexaboride CaB_6 and lanthanum doped calcium hexaboride $Ca_{1-x}La_xB_6$ ($x = 0.0051$) single crystals were measured by using a SQUID magnetometer up to fields of 55 kG.

The obtained crystals were less than several mm in size and 0.2–1 mm thick. The shapes were rectangular plate-like or cubic. The large crystals were shown in Fig. 1. The dope of lanthanum did not influence the size and shape of the CaB_6 crystals.

More than half of both the undoped and La-doped crystals were attracted or slightly moved by a magnet. Especially, the thin crystals were strongly attracted. The cubic crystals were hardly attracted. However, all the crystals were not attracted at all after being kept in HCl solution for a few hours.

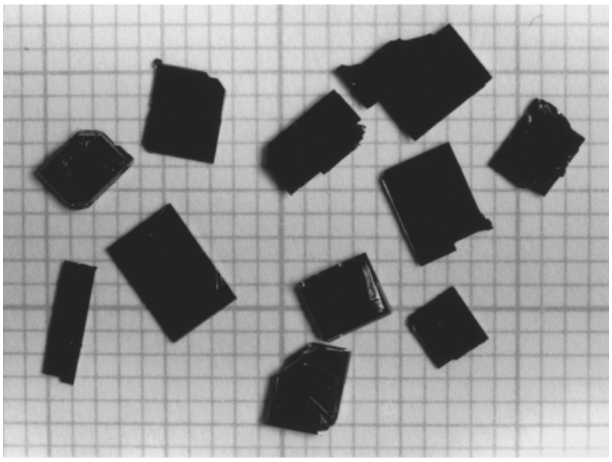

Fig. 1. As-grown CaB_6 crystals. One division is 1 mm.

Table I. Contents of iron impurity.

$Ca_{1-x}La_xB_6$ crystal		Fe (wt%)
$x = 0$	(as-grown)	0.019
	(HCl-treated)	<0.001
$x = 0.0051$	(as-grown)	0.010
	(HCl-treated)	0.001
Al	(flux)	0.003
CaB_6	(starting material)	0.002

Table I shows contents of iron impurity, which came from the aluminium flux. The undoped and La-doped CaB_6 crystals used for magnetic measurement contained 190 ppm and 100 ppm, respectively, before the HCl treatment. The iron was removed by the HCl treatment, which means that the iron existed on the surface of the CaB_6 crystals. This phenomena can be understood as follows. In the process of dissolving the aluminium flux by the NaOH solution, the aluminium matrix acts as a cathode. The crystals which are held on the surface of the aluminium acts as an anode and iron ions were reducted to iron on the crystal surface. That is, the crystals were electrochemically plated with iron. Consequently, the crystals were covered with iron because iron is stable in the NaOH solution. The iron was removed in the HCl treatment because iron reacts with HCl solution.

The magnetization of lanthanum doped calcium hexaboride $Ca_{0.0049}La_{0.0051}B_6$ at 300 K is shown in Fig. 2. Similar to what has been reported previously,[1)] a weak ferromagnetism is observed with hysteresis. The lanthanum doping of ~0.51% of our sample is close to the stoichiometry reported[1)] for the sample exhibiting the largest magnitude of ferromagnetic component. The magnitude of ferromagnetism (~2 emu/mol f.u.) is comparable to that reported previously. However, we find that by washing these samples

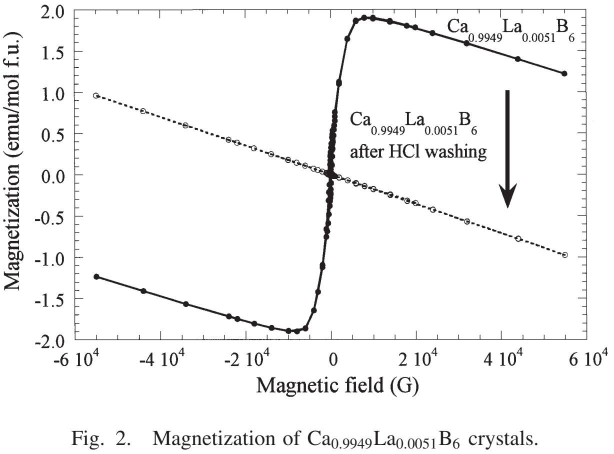

Fig. 2. Magnetization of $Ca_{0.9949}La_{0.0051}B_6$ crystals.

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in HCl the ferromagnetism disappears and the magnetism becomes diamagnetic (Fig. 2). As mentioned above, we have conducted chemical analysis on our samples and find an iron concentration of 0.010 wt% for $Ca_{0.9949}La_{0.0051}B_6$. The iron concentration after washing is 0.001 wt% while the lanthanum concentration does not change. Therefore, it is strongly indicated that the ferromagnetism originates from the iron impurities rather than being an effect of the lanthanum doping of CaB_6.

We have found that all the CaB_6 related samples treated with NaOH for the removal of flux (which is the method employed by previous researchers[1,5]) with or without lanthanum doping exhibit a ferromagnetic moment when sufficient thin crystals were added to the sample batch measured. In other words, the magnetism was sample dependent, with thin single crystals having a larger ratio of the ferromagnetism, which agrees with the idea that iron impurities are electrochemically plated onto the crystal surface during the NaOH treatment.

For example, the magnetization of CaB_6 is shown in Fig. 3 and it has ferromagnetism which disappears after washing. For the measurements given here, more than 10 crystals of CaB_6 and $Ca_{1-x}La_xB_6$ ($x = 0.0051$) were used with a typical total weight of 100 mg. The CaB_6 crystals used for measurements had a tendency to be thinner which accounts for the larger relative magnetic moment.

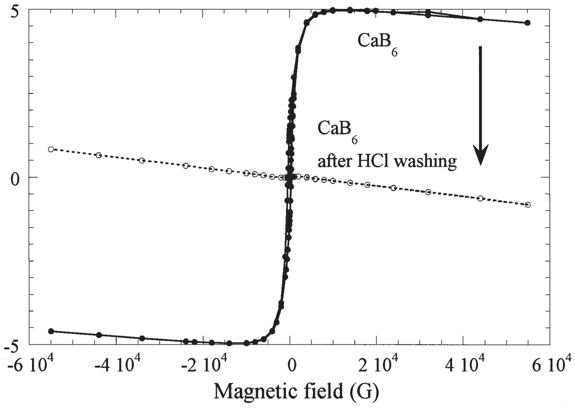

Fig. 3. Magnetization of CaB_6 crystals.

It should also be noted that we have investigated the magnetism of CaB_2C_2, which has similarities to CaB_6 and has previously been reported to exhibit ferromagnetism at room temperature.[6] On preparing a pure sample with iron concentration of less than 0.001 wt%, we find that the magnetism is diamagnetic[7] and it should be considered that the ferromagnetism observed in that system is also due to iron impurities since the results of analysis have not been presented in the previous studies.

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