Influence of Rb, Cs and Ba on Superconductivity of Magnesium Diboride.

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Magnesium diboride has been thermally treated in the presence of Rb, Cs, and Ba. Magnetic susceptibility shows onsets of superconductivity in the resulting samples at 52 K (Rb), 58 K (Cs) and 45 K (Ba). Room-temperature $^{11}$B NMR indicates to cubic symmetry of the electric field gradient at boron site for the samples reacted with Rb and Cs, in contrast to the axial symmetry in the initial MgB$_2$ and in the sample treated with Ba.

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Recent discovery of superconductivity in magnesium diboride, MgB$_2$, with $T_c \simeq 39$ K [1] has stimulated intensive study of this material. Its simple chemical composition, high symmetry of crystal lattice ($P6/mmm$) and hence high symmetric electronic structure [2] have enabled to clarify the mechanism of high temperature superconductivity in MgB$_2$ [3].

It has been reported previously that doping MgB$_2$ with carbon [4], Li [5, 6], Be [7], Zn [8], Al [6, 9], Ti [10], Ni, Fe, Co [11], Mn [12], and Si [8] only reduces the superconducting transition temperature. No information has been reported so far about doping of MgB$_2$ with heavier alkali and alkali-earth metals. These elements are capable of strong carrier donation to the electron system and may therefore essentially enhance superconducting properties of the host material. In this paper we report on the influence of Rb, Cs and Ba on superconductivity of MgB$_2$.

MgB$_2$ was thermally treated with Rb, Cs and Ba through liquid-phase reaction. The reacted samples are hereafter nicknamed as &Rb, &Cs, and &Ba samples. Two types of initial material were used: One contained 0.2-1 mm size granules of sintered in 1:1 molar ratio mixture of MgB$_2$ and Mg (MgB$_2$/Mg). The other one was fine powder of pure MgB$_2$. The initial material was vacuum sealed with the abundance of the metal (Rb, Cs or Ba) in quartz ampules preliminarily evacuated down to $10^{-3}$ Torr. The reactions were held with Rb and Cs for 10-100 hours at 160-300°C, and with Ba for 5 minutes at 700°C.

Superconductivity of the samples was studied by measuring the magnetic susceptibility, $\chi$, in temperature interval 4.2-300 K. The low-frequency ac susceptibility was measured using a home-made set-up by means of a mutual inductance technique at frequency 623 Hz in a driving field $\sim$0.1 Oe. The signal corresponding to the real part of $\chi$ was detected using a lock-in amplifier. Superconducting transitions of led, niobium, and BiSCO:2212 ($T_c=90$ K) were used to insure fidelity of the temperature scale of the measurements, as well as for calibration of the diamagnetic response. In the case of Rb the measurements were made without unsealing the ampules to avoid sample oxidation. It also enabled to consecutively alter heat treatment and measurement on the same batch. The unreacted excess of the metal heat-linked the particles of the sample and the walls of the vacuumized ampule to provide correct measurement of the sample temperature.

To track the changes in the superconducting properties during the treatment of MgB$_2$ with an alkali metal, the reaction with Rb was performed through portions of heat treatment alternated by susceptibility measurements. Each time two samples were simultaneously exposed to the heat treatment, one containing MgB$_2$/Mg and the other one with pure MgB$_2$. Temperature dependencies of magnetic susceptibility, $\chi(T)$, measured between consecutive portions of heat treatment on MgB$_2$/Mg with Rb, are shown in Figure 1a. $\chi(T)$ of the host MgB$_2$/Mg sample before the heat treatment, depicted in curve 1, has a sharp drop at 39 K denoting the superconducting transition at this temperature. Both the onset temperature and the width of the transition coincide with those of pure MgB$_2$. Subsequent heat treatments with Rb lead to first increase of the transition onset temperature up to 52 K (curves 2 through 4), and then rollback to 44 K (curves 5 through 7) [13]. The sample that initially contained pure MgB$_2$ powder has retained the superconducting transition at $\approx$39 K during the whole sequence of heat treatment. Hence under the applied conditions of thermal treatment, admixture of Mg to MgB$_2$ plays the key role in formation of the superconducting phase with $T_c$ higher than in the host MgB$_2$.

Relying on the above results, the heat treatment regimes were adjusted for the reactions of MgB$_2$/Mg with Cs and Ba. Fig. 1b shows $\chi(T)$ plots for &Cs and &Ba samples, as well as $\chi(T)$ for the initial MgB$_2$/Mg and for the &Rb sample. The $\chi(T)$ curves for &Cs and &Ba samples in Fig. 1b deviate towards the diamagnetic state below 58 K and 45 K, respectively, indicating the onsets of superconductivity. Therefore the superconducting transition temperature of the host MgB$_2$/Mg can be essentially enhanced through the reaction with Rb, Cs, or Ba.

The samples characterized in Fig. 1b were subjected to $^{11}$B NMR. The spectra were taken at room temperature in 7 T field using a Bruker MSL-300 spectrometer by means of the standard spin-echo technique with $\pi$ pulse.

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FIG. 1: Temperature dependencies of magnetic susceptibility: (a) measured between consecutive heat treatments of MgB$_2$/Mg with Rb, 1 – initial sample, 2 – 10 hours at 180°C, 3 – 13 hours at 190°C, 4 – 15.5 hours at 200°C, 5 – 36 hours at 200°C, 6 – 56 hours at 200°C, 7 – 18 hours at 300°C; (b) the initial MgB$_2$/Mg, the one reacted with Ba (5 min. at 700°C), with Rb (17 hours at 200°C), and with Cs (20 hours at 160°C followed by 100 hours annealing at 100°C). Arrows indicate onsets of superconducting transitions.

FIG. 2: Room-temperature $^{11}$B NMR spectra at 7 T in the host MgB$_2$/Mg and in MgB$_2$/Mg reacted with Ba, Cs, and Rb: The spectra in whole (a) and details of the central peaks (b).
been found for the samples that initially contained 1:1 mixture of MgB$_2$ and Mg. Room-temperature $^{11}$B NMR has indicated to the presence of a phase with cubic symmetry of charge environment at boron site in the samples reacted with Rb and Cs, in contrast to the axially symmetric cases for the host MgB$_2$ and for the sample reacted with Ba.

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