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Formation of nanocrystalline MgB_2 under high pressure

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Abstract

The microstructural features of MgB_2 at ambient pressure and high pressure have been investigated by means of *in situ* synchrotron radiation x-ray diffraction and transmission electron microscopy (TEM). The x-ray diffraction measurements indicated that nanocrystalline MgB_2 formed in the pressure range of 26.3–30.2 GPa. TEM investigations reveal complex structure domains with evident lattice distortion in the relevant samples. The superconductivity of nanocrystalline MgB_2 was measured and compared with that of the starting sample of MgB_2.

The recently discovered binary boride system with the stoichiometry MgB_2 has attracted considerable interest due to its superconductivity at the temperature of 39 K [1]. At ambient pressure, this compound adopts a layered hexagonal crystal structure and exhibits metallic conductivity [2, 3]. The effect of a boron isotope on MgB_2 indicated that this material is a conventional phonon-mediated BCS superconductor [4]; therefore, pressure will definitely affect its superconductivity. A number of investigations of MgB_2 have been carried out addressing various aspects including further improvement of the superconducting transition temperature through choice of doping element [5] and the dependences of the superconductivity [6–8], band structure [9–11] and lattice parameters [12–14] on pressure. However, most of the experimental results were obtained at ambient pressure or at pressure below 15 GPa; little work has been performed on this material under higher pressures. In this paper, we report an investigation of the structural change induced by high pressure in MgB_2. *In situ* synchrotron radiation x-ray diffraction (SR-XRD) measurements under high pressure up to 42.2 GPa and the transmission electron microscopy (TEM) observations for the compressed samples show that the pressure of 30.2 GPa could induce the formation of nanocrystalline MgB_2. The parallel superconducting transition temperature is also measured; it shows a negative shift with increasing pressure.

The samples were synthesized by direct reaction of magnesium chips and boron powder with nominal purities of 99.5 and 99.99% respectively. A mixture of magnesium and boron

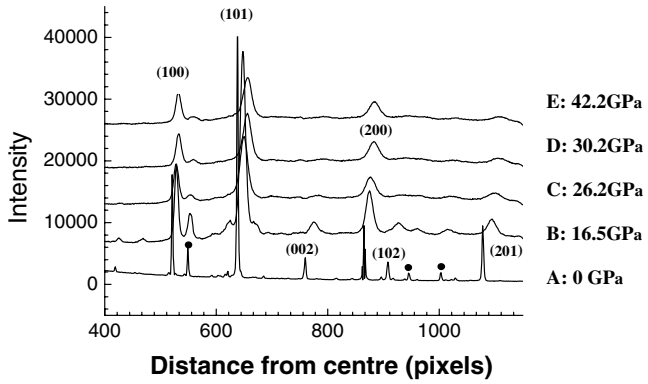

Figure 1. SR-XRD patterns of MgB_2 under ambient pressure and high pressures, showing an obvious microstructural change at 30.2 GPa. The peaks marked by solid circles are from the metal gasket.

with the given stoichiometry was pressed into pellets, then placed in a tantalum foil and sealed into a quartz ampoule after pressure had been reduced to 1.7×10^{-5} Torr. The ampoule was put into a tube-type furnace and heated to 950 °C for 3 h, and thereafter cooled to room temperature in the air. The synthesized sample was identified by the powder x-ray diffraction method as being single phase, as all peaks for the sample can be indexed in terms of the hexagonal unit cell with $a = 0.308$ nm and $c = 0.352$ nm. The magnetization measurements confirmed a transition temperature for the sharp superconducting onset at 39 K.

In situ x-ray diffraction (XRD) measurements in a diamond anvil cell (DAC) were performed at the Photon Factory in Japan [15]. In the experiments, the wavelength of the x-rays was monochromatized to 0.06198 nm and the applied pressure was determined by using the fluorescence of ruby chips embedded in the sample. A mixture of methanol, ethanol and water in the proportions 16:4:1 was used as the pressure-transmitting medium. XRD data for the fine powder sample were recorded on an imaging plate [16] with an exposure time of 20 min by using a collimator of $\varnothing 30$ μm. All measurements were performed at room temperature. The characterization of samples was carried out using H-9000 NA electron microscope. Samples that had and had not undergone high-pressure treatments were ground mechanically in a mortar before TEM observation; after that they were each placed on a copper grid. The magnetizations of MgB_2 at ambient pressure and high pressure were measured using a vibrating-sample magnetometer.

Figure 1 shows SR-XRD patterns of MgB_2 under applied pressures up to 42.2 GPa. It was found that all diffraction peaks of the sample treated at various pressures shift to the right; this means that the pixels get larger (i.e. the 2θ value becomes larger), implying a reduction of the lattice parameters under high pressure. In particular, the intensity of the diffraction peaks became much suppressed with increasing pressure. The (101) peak (curve A in figure 1) is very sharp at ambient pressure, but becomes broad and blunt in the pressure range of 26.3–30.2 GPa. This provides evidence for a structural change occurring within this pressure range. In order to facilitate interpretation of the experimental evidence on microstructural changes under high pressure, the dependence of the full width at half-maximum (FWHM) of the XRD peak (101) on pressure was obtained; this is shown in figure 2. It can be seen that the FWHM of the (101) peak dramatically increased with increasing pressure. The FWHM at 30.2 GPa is approximately 9.7 times as high as that at ambient pressure, revealing that the pressure plays a vital role in the microstructural change of MgB_2.

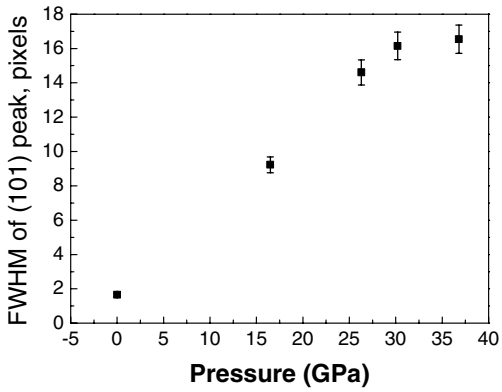

Figure 2. The dependence of the FWHM of the XRD peak (101) on pressure, showing the significant increase of the FWHM with increasing pressure.

The identifications of the intrinsic characteristics for compressed and uncompressed samples were performed by means of TEM investigations. Figure 3(a) shows a TEM image of the sample prepared at ambient pressure. The average grain size of the crystal in this sample is about 0.6 μm, as reported by Li *et al* [17]. Figure 3(b) illustrates the microstructural features resulting from an applied pressure of 30.2 GPa. Unlike in the starting MgB_2, a number of strip-like regions with apparent structural distortion can be clearly recognized. In these areas, the long-range order in the crystal structure has been seriously damaged by the applied high pressure. Systematic analyses indicate that the crystalline grains become ultrafine with an average size of about 25 nm in these compressed samples, as shown in the inset of figure 3. This observation is in good agreement with x-ray data, showing apparently broad reflection peaks in the high-pressure range of 20.6–30.2 GPa. The electron diffraction analysis also confirms that there is a significant lattice distortion in the compressed sample and the lattice parameter greatly depends on the applied pressure. At 30.2 GPa, the reduction in the *c*-axis direction is more than three times that in the *a*-axis direction in the layered hexagonal structure of MgB_2, suggesting that the bonding within the boron layers is stronger than that between boron layers [18].

The superconductivity of the nanocrystalline MgB_2 powder produced under 30.2 GPa was investigated by using a vibrating-sample magnetometer in a field of 30 Oe. Figure 4 shows the temperature-dependent susceptibility of the nanocrystalline MgB_2. Comparing with that of MgB_2 prepared under ambient pressure, it is clearly seen that the transition temperature for the onset of nanocrystalline MgB_2 drops to 35 K and that its transition width is significantly broadened, resembling the transition process of a granular superconductor. Taking the fact that the lattice distortion will be partially reversed after decompression into account, we believe that the real T_c of MgB_2 subjected to 30.2 GPa should be slightly smaller than the result obtained in this work.

In conclusion, the effect of high pressure on the microstructure and superconducting transition temperature in MgB_2 has been investigated by means of SR-XRD measurements in a DAC and by TEM. In the XRD analysis and TEM observation, no phase transition was observed at high pressure below 42.2 GPa. At 30.2 GPa, a great deal of nanocrystalline MgB_2 was formed. The magnetization measurements confirm the transition temperature for the onset of superconductivity of nanocrystalline MgB_2 to be about 35 K.

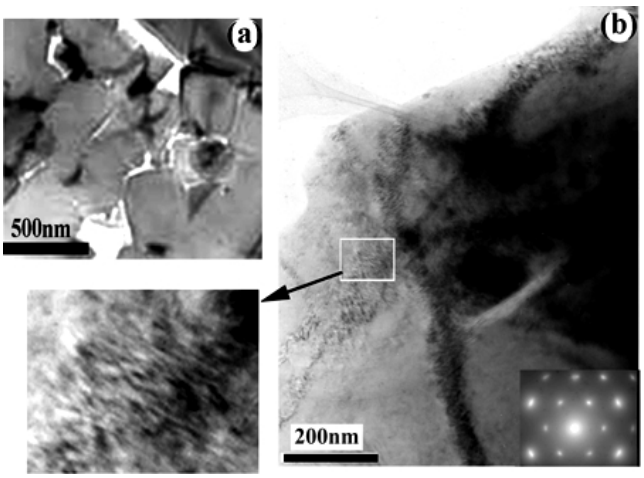

Figure 3. TEM images showing the essential microstructure of (a) a sample prepared at ambient pressure and (b) a sample subjected to the high pressure of 30.2 GPa.

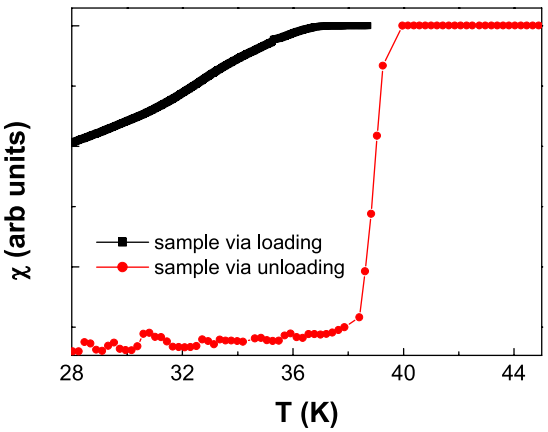

Figure 4. Magnetization of MgB_2 as a function of temperature and pressure. The solid circles represent the magnetization of the starting MgB_2 and the squares represent the magnetization of sample obtained via high-pressure treatment at 30.2 GPa.

(This figure is in colour only in the electronic version)

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