# Low Temperature Synthesis and Characterization of Cubic $CaB_6$ Ultrafine Powders

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Ultrafine calcium hexaboride ($CaB_6$) powder was successfully synthesized at 500 °C in an autoclave by using $CaCl_2$ and $NaBH_4$ as the reactants. X-ray powder diffraction pattern and Raman spectra indicate the formation of $CaB_6$. The atomic ratio of B to C of 5.91:1.0 was determined from X-ray photoelectron spectra.

Calcium hexaboride, $CaB_6$, is an important material due to its large electrical conductivity, moderate hardness, high chemical stability, and high melting point (2373 K).[1–3] $CaB_6$ has been applied widely in many areas. For example, $CaB_6$ can serve as a high temperature material, surface protection, and wear resistant material. Recently, the unexpected discovery of ferromagnetic order at a very high Curie temperature ($T_c$ ca. 600 K) in lightly La doped $CaB_6$ has been reported by Young et al.[4] This new property has initiated a great deal of interest in this material[5–8] because $Ca_{1-x}La_xB_6$ has no partially filled *d*- or *f*- orbits, which are usually required for magnetism.

Traditionally, cubic calcium hexaboride was prepared by various high temperature reactions such as the direct combination of boron with calcium (ca. 1000 °C);[9] reaction between $Ca(OH)_2$ and B in vacuum (above 1700 °C);[10] carbothermal reduction of $CaCO_3$ and $B_4C$ (above 1600 °C) in vacuum,[11] and so forth.

In this paper, we report a low temperature chemical route to synthesize ultrafine $CaB_6$ with a yield of about 95%. The reaction was carried out in an autoclave and can be described as follows:

$$CaCl_2 + 6NaBH_4 \rightarrow CaB_6 + 2NaCl + 12H_2 + 4Na$$

In a typical procedure, an appropriate amount of anhydrous $CaCl_2$ (2.22 g) and $NaBH_4$ (4.54 g) were put into a stainless autoclave of 50-mL capacity. The autoclave was sealed and maintained at 500 °C for 8 h, then cooled to room temperature naturally. The product was firstly washed with absolute ethanol to remove the produced Na, and then washed with distilled water to remove NaCl and other impurities. After drying in vacuum at 60 °C for 4 h, the final gray powder product was obtained.

X-ray powder diffraction (XRD) was carried out on a Rigaku Dmax-$\gamma$ A X-ray diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.54178$ Å). The morphology of the product was observed from transmission electron microscopy (TEM) images taken with Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K$\alpha$ X-ray as the excitation source. Raman spectra were measured on a LABRAM-HR Raman spectrophotometer. The 514.5-nm laser was used as an excitation light source. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) profiles were collected with Shimadzu-50 thermoanalyzer apparatus under airflow.

Figure 1 shows the XRD pattern of the as-prepared $CaB_6$ sample, all the peaks can be indexed as cubic $CaB_6$. After refinement, the lattice constants, $a = 4.132$ Å, is very close to the reported value for $CaB_6$ ($a = 4.150$ Å, JCPDS-ICDD card, No. 741171).

The wide scan XPS spectrum of as-prepared $CaB_6$ sample indicated the presence of B and Ca. It is found from the XPS spectra (not shown) that the binding energy of B 1s is at 192.6 eV and Ca $2p^3$ is at 348.2 eV. The qualification of the peak intensities reveals that the atomic ratio of B to Ca is 5.91:1.0, which is close to the chemical stoichiometric relation between B and Ca.

Figure 2 shows a typical TEM image of the as-prepared $CaB_6$. The sample has a cubic morphology with an average size of 180 nm. The inset of Figure 2 shows the selected area electron diffraction pattern of $CaB_6$, which is consistent with the high crystallinity of cubic $CaB_6$.

Figure 3 shows the Raman spectra of the as-prepared $CaB_6$

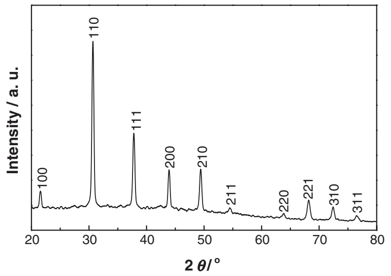

**Figure 1.** XRD patterns of the $CaB_6$ sample.

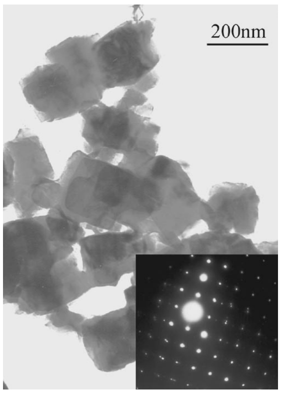

**Figure 2.** TEM image of the $CaB_6$ sample. Inset: Selected area electron diffraction pattern of $CaB_6$.

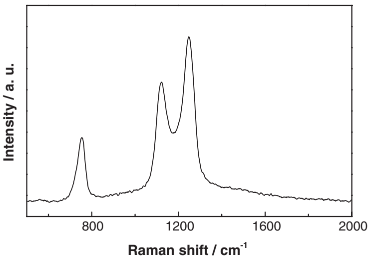

**Figure 3.** Raman spectra of the $CaB_6$ sample at room temperature.

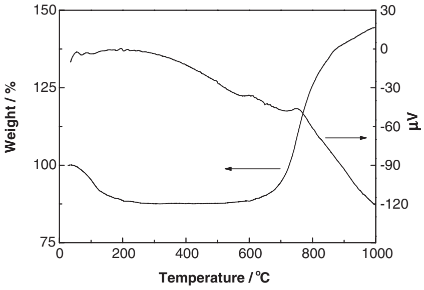

**Figure 4.** TGA and DTA curves for $CaB_6$ sample.

sample at room temperature. Three peaks at 754.3, 1121.8, and 1246.9 $cm^{-1}$ could be observed clearly, which is attributed to Raman active modes $A_{1g}$, $E_g$, and $T_{2g}$ for $CaB_6$, respectively.[12] The Raman peaks of the as-prepared $CaB_6$ sample are broader than that of the $CaB_6$ single crystal grown by floating-zone method, which may be due to disorders induced by the existence of defects and strains in ultrafine materials.[12]

Figure 4 shows the TGA and DTA curves of the $CaB_6$. It can be seen that a pronounced weight gain step occurred in the temperature range of 526 to 995 °C, which can be attributed to the oxidation of $CaB_6$. Two exothermic peaks at 608 and 753 °C can be observed in the DTA curve. This suggests that the oxidation of $CaB_6$ is composed of two steps, which has been reported for $CaB_6$.[1] A small weight loss step can also be observed around 100 °C, which may arise from the evaporation of absorbed water on the surface of the sample. The TGA and DTA data reveal that the initial oxidation temperature for ultrafine $CaB_6$ is 526 °C, which is much lower than that of $CaB_6$ with larger size (median particle size $= 8\,\mu m$).[1] The decrease of oxidation resistance for ultrafine $CaB_6$ may be due to its small grain size. The ratio of the surface to volume increases remarkably when the particle size decreases. This will lead to more defects and strains exposed on the crystal surface, which is not beneficial to oxidation resistance.

In the present route, no $CaB_6$ could be detected in the product if the temperature is below 450 °C. Heating at a higher temperature such as 600 °C will result in an obvious increase of the crystalline $CaB_6$ sizes. An optimum temperature for ultrafine $CaB_6$ is about 500 °C. A reaction time at 500 °C in the range of 3–10 h did not significantly affect the crystallite size. If the time is shorter than 2 h, the reaction becomes very incomplete and the crystallinity is very poor due to too short reaction time. One feature of this synthesis route is the high pressure in the autoclave, coming from the produced $H_2$ (about 30 $kg/cm^2$ estimated by the ideal gas law). The high pressure makes the crystalline $CaB_6$ form at a relatively low temperature.

In summary, the ultrafine $CaB_6$ powder was successfully synthesized using $CaCl_2$ and $NaBH_4$ as the reactants at a low temperature of 500 °C. The products mainly consisted of cubic particles with an average size of 180 nm. This route allows for the facile formation of $CaB_6$ at a low temperature, and may be extended to synthesis other borides.

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