Preparation of Plywood-like Fe₃BO₅ Nanorods by a Facile Hydrothermal Method at Low Temperature

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Single-crystal plywood-like vonsenite (Fe_3BO_5) nanorods were prepared through a facile hydrothermal method at 140 °C for 40 h with $K_4Fe(CN)_6$ and $NaBH_4$ as starting materials. The Fe_3BO_5 nanorods, which are composed of 5 to 7 nanobelts, have a diameter of about 250 nm and length ranging from 7 to 15 μm. The nanorods are identified to grow along the [001] direction. On the basis of the results, the formation process of the Fe_3BO_5 nanorods is discussed. The magnetic measurement indicates that $T_N = 140$ K.

Vonsenite (Fe_3BO_5) belongs to the family of ludwigites with chemical formula $M^{II}_2M'^{III}BO_5$, where M and M' are divalent and trivalent 3d metal ions, respectively. These compounds of the ludwigite family show many interesting properties. For example, they are promising catalysts for redox catalytic reactions because of the facile change of the oxidation state of their cations,[1] and they can be used as model compounds in studies of the mechanisms of electron interactions in transition-metal oxides because of their mixed valency.[2] The homometallic Fe_2FeBO_5 has interesting electronic and magnetic properties[3–6] because it presents positional order and the electrons may delocalize within the two-dimensional structures (called the walls). In fact, the conductivity of Fe_2FeBO_5 is much higher than that of the mixed ludwigites (M' = Fe, M = Cu and Ni).[7,8]

Solid-state synthesis is the conventional way to synthesize Fe_3BO_5 by heating a stoichiometric mixture of iron oxide and boron oxide at high temperature.[3,5,9,10] A hydrothermal method has been reported to prepare Fe_3BO_5 at 680 °C.[11] However, these methods are not economical and facile because they need high temperature and complicated equipment. Herein, we propose a facile method to synthesize Fe_3BO_5 at low temperature. The Fe_3BO_5 plywood-like nanorods were obtained for the first time by using $K_4Fe(CN)_6$ and $NaBH_4$ as starting materials. Such an approach provides a new approach for large-scale synthesis of Fe_3BO_5. It becomes possible to synthesize of Fe_3BO_5 at low temperature.

In a typical process, Fe_3BO_5 nanorods were obtained as follows: 0.5 g of potassium ferrocyanide ($K_4Fe(CN)_6$) and 7.5 g of sodium borohydride ($NaBH_4$) were dissolved in 30 mL of distilled water. The mixed solution was vigorously stirred with a magnetic stirrer at room temperature for 10 min. After that, the precursor solution was transferred into a Teflon-lined stainless steel autoclave with 40-mL capacity. The autoclave was subsequently sealed tightly and maintained at 140 °C for 40 h. After the reaction was completed, the autoclave was allowed to cool to room temperature. The resulting gray precipitates were separated with a centrifuge, and the collected precipitates were washed with distilled water and alcohol three times, respectively. Finally, the gray products were dried in a vacuum oven at
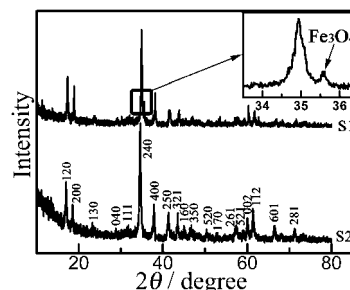

Figure 1. XRD patterns of as-prepared sample.

40 °C (labeled S1).

The powder X-ray (Cu Kα) diffraction (XRD) patterns of the as-prepared samples are shown in Figure 1. The inset is an expanded pattern of S1 from $2\theta = 34$ to 36°. As shown in the inset, there is a peak at $2\theta = 35.5°$, which is the finger peak of magnetite (Fe_3O_4). It indicates that S1 is a mixture of Fe_3BO_5 (JCPDS 25-0395) and Fe_3O_4 (JCPDS 16-0629). It is well known that Fe_3O_4 is ferromagnetic and Fe_3BO_5 is paramagnetic at room temperature. So, pure Fe_3BO_5 can be obtained by operating magnet separation. Firstly, the mixture was dispersed in ethanol by ultrasonication. The suspension was separated subsequently by applying a permanent NdFeB magnet. Then, the top suspension was collected. This process was repeated three times at least. The ultimate gray suspension was put into a centrifugal test tube and was centrifugated for 5 min at 4000 rpm. Finally, the resulting gray powders were dried in a vacuum oven at 40 °C (labeled S2). The XRD patterns of S2 showed that all diffraction peaks are consistent with the standard card of Fe_3BO_5, and no Fe_3O_4 peaks were observed, which indicates that the ultimate gray powers are pure Fe_3BO_5 (orthorhombic crystal system, space group *Pbam* [55], $a = 9.452$ Å, $b = 12.28$ Å, $c = 3.072$ Å).

The field emission scanning electron microscopy (FESEM) images of as-prepared samples are shown in Figure 2. Figure 2a shows large quantities of nanorods with length of 7 to 15 μm. These rods arrange like many urchins with a uniform diameter of 20–30 μm. It is also noticed that a few octahedrons present among urchin-like clusters, exhibiting that S1 is a mixture which has been proved by the XRD pattern in Figure 1. Figure 2b shows a magnified cluster which exhibits the cluster having an urchin structure. The morphology of S2 is showed in Figure 2d, it is noticed clearly that nanorods are distributed disorderedly (urchin-like structure is destroyed) and that no octahedron is observed. It indicates that the pure Fe_3BO_5 was obtained after magnetic separation. Figures 2c and 2e show the magnified SEM images of S1 and S2, respectively. They reveal that a typical nanorod has a diameter of about 250 nm, and that the nanorod has a plywood-like structure composed of 5 to 7 nanobelts. The
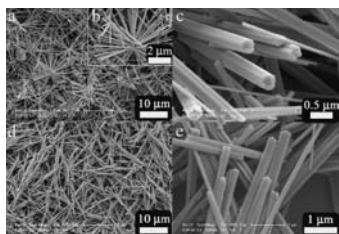
Figure 2. HESEM images of as-prepared samples: (a) S1; (b) a single Fe_3BO_5 cluster of S1; (c) the typical nanorod of S1; (d) S2; (e) the typical nanorod of S2.
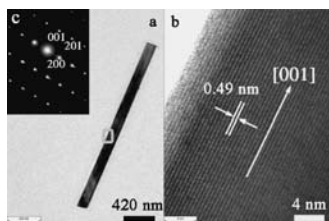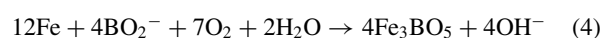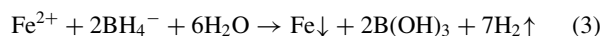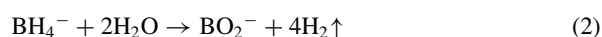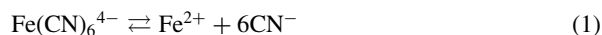

Figure 3. (a) Representative TEM image of Fe_3BO_5 nanorod; (b) HRTEM image of the rod (boxed area in (a)); (c) SAED pattern of a individual Fe_3BO_5 rod.

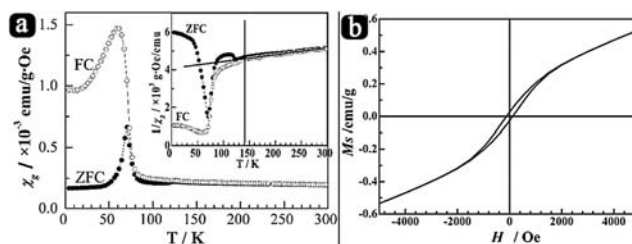**Figure 4.** (a) χ_g–T curves in ZFC and FC modes for Fe_3BO_5 nanorods at an applied magnetic of 0.1 T. Inset: $1/\chi_g$–T curves. (b) Magnetic hysteresis loop at 300 K.

plywood-like structure is stable and can not be destroyed by sonication. It is suggested that the plywood-like structure grows homoepitaxially rather than adhering to each long and thin nanocrystal because of the orderly surfaces of plywood-like nanorods and the stable plywood-like structure which can not be destroyed by sonication. Firstly, a layer of Fe_3BO_5 is formed. Then, another layer grows on the first layer. Finally, the plywood-like Fe_3BO_5 nanorod forms layer-by-layer.

Further observations on the structure of Fe_3BO_5 were conducted by high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED). A representative TEM image of a Fe_3BO_5 nanorod is shown in Figure 3a. Figure 3b shows the SAED pattern obtained along a typical individual nanorod. The ED reveals that the nanorod is single crystal and can be indexed as (200) and (001) planes of Fe_3BO_5. The HRTEM analysis provides more detailed structure information of the Fe_3BO_5 nanorods (Figure 3c). It further confirms the single-crystal nature of Fe_3BO_5 nanorod. The lattice fringe observed in this image is 0.49 nm, which corresponds to the interplanar spacing of the (200) plane. Combined with the ED results, it is reasonably concluded that the preferred growth of nanorods is along [001], the c axis of Fe_3BO_5 crystal.

The $NaBH_4$ plays an important role in the formation of Fe_3BO_5. When the amount of $NaBH_4$ is decreased, or NaOH is added, in the reaction system, more octahedral magnetites were obtained. The suggested reaction equations in our system are as follows:

$$Fe(CN)_6{}^{4-} \rightleftarrows Fe^{2+} + 6CN^- \tag{1}$$

$$BH_4{}^- + 2H_2O \rightarrow BO_2{}^- + 4H_2\uparrow \tag{2}$$

$$Fe^{2+} + 2BH_4{}^- + 6H_2O \rightarrow Fe\downarrow + 2B(OH)_3 + 7H_2\uparrow \tag{3}$$

$$12Fe + 4BO_2{}^- + 7O_2 + 2H_2O \rightarrow 4Fe_3BO_5 + 4OH^- \tag{4}$$

Magnetic susceptibility measurements in an applied magnetic field of 1 kOe in zero-field-cooling (ZFC) and in field-cooling (FC) modes are shown in Figure 4a. The plot of the inverse susceptibility $(1/\chi_g)$ as a function of temperature (inset of Figure 4a) shows that $T_N = 140$ K, which is higher than the value of the corresponding solid mass.[9] Hydrothermal method is advantage to synthesize materials with fewer defects comparing with solid-state reaction. The fewer defects can enhance superexchange interaction among ions, which may be responsible for the increase of T_N. The $1/\chi_g$ of ZFC exhibits a weak broad peak at $T = 81$–121 K, which can be explained by the existence of Fe_3O_4 (Figure 4b).[12] The ZFC and FC susceptibility show a hysteresis behavior below 80 K, which is similar to the report.[9]

In conclusion, single-crystal vonsenite nanorods with plywood-like structure have been obtained through a facile hydrothermal approach at low temperature by using $K_4Fe(CN)_6$ and $NaBH_4$ as staring materials. Excessively consumed $NaBH_4$ was found to be responsible for the formation of vonsenite. The plywood-like nanorods composed of 5 to 7 nanobelts formed by layer-by-layer epitaxial growth. The enhanced T_N may be attributed to the increase of superexchange interaction. Such an approach provides a new approach for large-scale synthesis of Fe_3BO_5 at low temperature.

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