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Hydrothermal synthesis and magnetic property of NaV_2O_5 nanorods①

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[Abstract] One-dimensional rod-like NaV_2O_5 was synthesized by hydrothermal method, which draws much attention as an exotic spin-Peierls compound. The samples have been characterized by X-ray diffraction (XRD), transmission election microscopy (TEM), and magnetic susceptibility measurements. The pH value and the reducing agent are critical for synthesizing NaV_2O_5 nanorods. The reducing agent NH_2OH may play a key role in the assembly and growth of nanorods of products.

[Key words] nanostructures; chemical synthesis; magnetic properties
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1 INTRODUCTION

Recently, one-dimensional (1D) nanostrcture materials are the focus of considerable interest, since these materials show different physical and chemical properties to their bulk counterparts[1]. But well-defined structures of this scale are difficult to obtain because neither typical physical techniques nor planned chemical synthesis are very applicable in this size domain. So 1D nanostructure materials have been prepared recently by many advanced methods such as molecular-coordination template synthesis, polymer or carbon nanotube oriented synthesis[2~8]. The study of these materials can also help us to understand the mechanisms of the formation of 1D nanostructure and the growth process at atomic level.

NaV_2O_5 compound has recently received considerable attention because it appears to be the second inorganic material displaying spin-Peierls behavior in magnetic susceptibility measurement. The first one is $CuGeO_3$, whose critical temperature T_{sp}= 35.3 K is the highest of all known organic or inorganic spin-Peierls compounds[9~11]. Conventionally, NaV_2O_5 could be synthesized by traditional high-temperature solid-state reaction methods[11, 12]. The weighed mixtures with appropriate molar ratios of $NaVO_3$, V_2O_3 and V_2O_5 were heated at 650 ℃ in an evacuated silica tube for several days, because the target compound is a mixed-valence ($n(V^{4+})/n(V^{5+}) = 1$) oxide and is sensitive to atmospheric conditions. The starting reactant V_2O_3 should be prepared by reducing NH_4VO_3 in H_2 gas at 900 ℃ for 48 h.

Hydrothermal method has been widely used in the synthesis of novel transition metal oxides[13], zeolite materials and Keggin-type polyanions[14]. Hydrothermal methods was used to prepare new compounds of Mo, W and V oxides or bronzes by Whittingham et al[15]. Hagrman et al[16] synthesized a new metastable VO_2 phase hydrothermally. As noted by Boylan et al[17], the compound NaV_2O_5 can be obtained hydrothermally under acidic conditions using the tetramethylammonium ion as the reducing agent.

Hydroxylamine hydrochloride is a widely used reducing agent in organic synthesis in acidic solutions. Recently, it has been used to prepare reduced transition-metal oxides by soft chemical methods[18]. Rutile vanadium dioxide has been obtained with hydroxylamine hydrochloride in an aqueous solution reported by Manivanna et al[19].

Herein we first report an alkaline solution-based hydrothermal reaction with V_2O_5 and NaOH as starting agents, resulting in the formation of NaV_2O_5 nanorods with hydroxylamine hydrochloride as reductant and coordination agent. The magnetic properties, reaction factors and the mechanism of controlled synthesis of 1D nanorods have been studied.

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2 EXPERIMENTAL

NaOH (96%) and V_2O_5 (99%) were stoichiometrically added to a Teflon-lined stainless autoclave with a capacity of 100 mL, then the autoclave was filled with distilled water, stirred to an aqueous solution. Hydroxylamine hydrochloride was added into this solution, resulting in deep-colored solution due to the reduction of vanadium ion. The solution was filled with water up to about 80% of the total volume of the autoclave, adding HCl/NaOH to control the pH = 7.0~ 9.0. The molar ratio of V_2O_5, NaOH and $NH_2OH \cdot HCl$ was 1∶2∶1. The synthesis reaction equation is

$$V_2O_5 + 2NaOH + NH_2OH \cdot HCl \rightarrow NaV_2O_5 \downarrow + NaCl + 1/2N_2 \uparrow + 3H_2O \qquad (1)$$

The autoclave was maintained at 140 ℃ for three days and then cooled to room temperature. The solution was neither shaken nor stirred on heating. A black precipitate was collected and washed with water, then dried at 80 ℃. In this precipitate, nanorod crystals were found. The nature of the NaV_2O_5 phase formed strongly depends on the pH of the medium. We also used sodium vanadate ($NaVO_3 \cdot 2H_2O$ 96%) to synthesize NaV_2O_5, keeping other experimental variables unchanged, the product is the same as that obtained above. X-Ray powder diffraction (XRD) analysis was conducted on a Rigaku Dmax X-ray diffractometer at a scanning rate of 0.05(°)/s with 2θ ranging from 10° to 70° using graphic monochoromatic Cu K_α radiation (λ= 1.540 2 Å), A transmission electron microscope (TEM) at 200 kV was employed to characterize the morphology of products. Images were collected in a bright field. Copper grids (300 mesh) coated with an amorphous carbon film were obtained commercially. Samples were prepared by placing drops of diluted ethanol dispersed of nanocrystallites on the surface of grids. Electron dispersive spectroscopy (EDS) was utilized to analyze the composition and oxidation state. The magnetic susceptibility (χ) was measured using a vibrational sample magnetometer (Lakeshore) in the temperature range from 2 K to room temperature.

3 RESULTS AND DISCUSSION

Fig. 1(a) shows the X-ray powder diffraction (XRD) pattern for the sample of NaV_2O_5 obtained under alkaline condition. All peaks can be indexed to an orthorhombic structure with lattice parameters of a= 11.293 Å, b= 3.606 Å, and c= 4.798 Å. It is consistent with the previous result reported by Isobe and Ueda[11]. This suggests the formation of single-phase NaV_2O_5 without any trace of impurities by hydrothermal synthesis.

Fig. 1(b) shows the X-ray powder diffraction (XRD) pattern for the sample of NaV_2O_5 obtained under acidic conditions. It is found that the dominant phase is the NaV_2O_5. But an impurity phase is found, which is identified to be $(NH_4)V_4O_{10}$. Thus, the nature of final product depends on the pH value in the reaction medium.

Through a series of experiments, it is found that

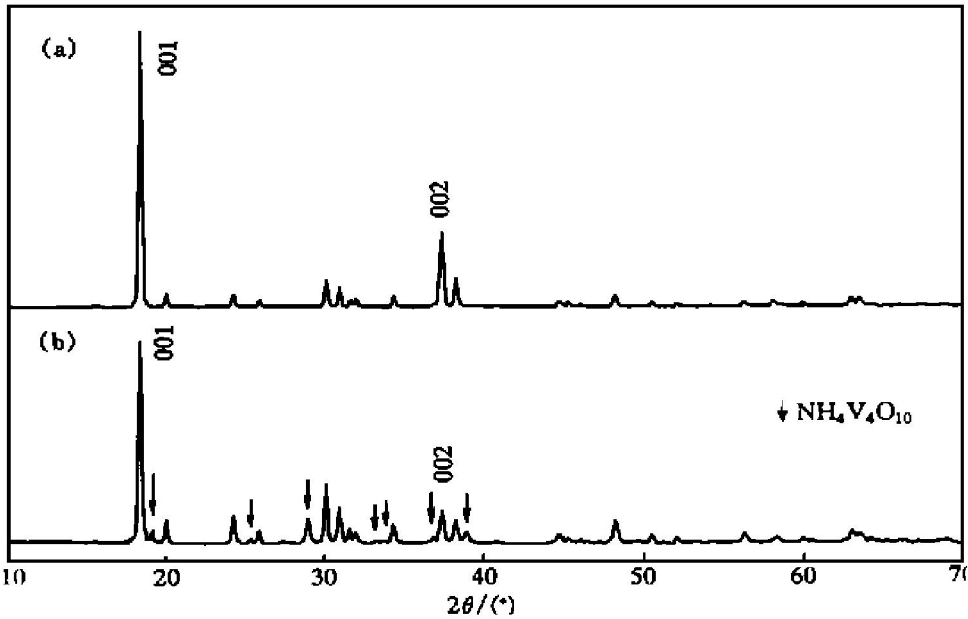

Fig. 1 X-Ray powder diffraction patterns for NaV_2O_5 prepared by hydrothermal method under different pH values

(The peaks marked by arrows arise from the impurity phase $(NH_4)V_4O_{10}$.)

(a) —pH= 8.3; (b) —pH= 6.4

the NaV_2O_5 product can be formed when the pH value is between 5. 5 and 9. 0. When the pH value is lower than about 5. 5, no NaV_2O_5 phase is observed, and only $(NH_4)V_4O_{10}$ phase is obtained. While pH value is larger than about 9. 0, no precipitate is observed. This suggests that the phase of NaV_2O_5 product can be obtained in the pH range of 5. 5~ 9. 0. It must be pointed out that pure NaV_2O_5 should be prepared in a weak alkaline solution in the pH value range of 7. 0~ 9. 0. While in acidic media, the final product is the mixture of NaV_2O_5 and $(NH_4)V_4O_{10}$. Boylan et al[17] reported that the NaV_2O_5 crystals were prepared hydrothermally only under acidic conditions using the tetramethylammonium ion as the reducing agent. It is not difficult to understand that an acidic oxide of V_2O_5 can dissolve in alkaline solution readily, and generates precipitate in acidic conditions. However, the present experimental results show that the weak alkaline condition is preferred to the acidic condition for preparing single phase NaV_2O_5. This is because in acidified medium other vanadium oxides form in a rapid rate, so with the controlling of the pH values of the solution, we can control different reactions.

In the XRD pattern shown in Fig. 1(a) there is a relatively stronger intensity for the (001) peak than expected from the results of refinement, which indicates a preferential orientation of (001) in the crystal NaV_2O_5. We inferred that the growth of NaV_2O_5 crystal was oriented. This inference was confirmed by TEM image shown in Fig. 2. It indicates that the NaV_2O_5 crystallites display rodlike morphology with a size of (1 600 mm~ 2 000 mm) × 120 nm, and the shape is uniform and regular. Chemical composition of the rodlike crystals was made by electron dispersive spectroscopy (EDS). EDS result shows that the composition is the same as NaV_2O_5.

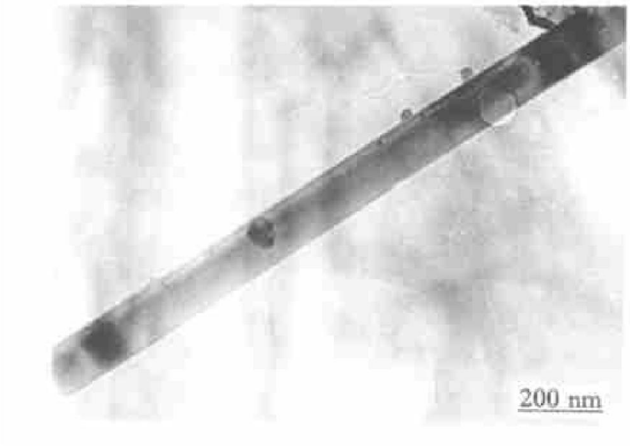

Fig. 2 TEM image of sample NaV_2O_5

As to the mechanism of formation of rod-like products of NaV_2O_5, the choice of NH_2OH is crucial. Nitrogen as well as oxygen in NH_2OH both can coordinate to center vanadium to give possible complex of $[V(NH_2OH)_2O_2]^+$, which adopts the octahedron configuration with a plane of center vanadium chelated by two hydroxylamines. These complexes may act as intermediates to pyrolysis and assembly along the direction of O—V—O and results in the orientation growth of crystallites of NaV_2O_5. Therefore, a mechanism of coordination-control template growth could be suggested to explain the formation of final products. In Ref. [17], the reducing agent $[N(CH_3)_4]^+$ provides no electron pair to coordinate to center cations.

Fig. 3 shows the temperature dependence of susceptibility for the sample prepared above at $H = 1$ T. The χ has a broad maximum at around room temperature, reflecting the low dimensional nature of the spin system and is consistent with the characteristics of the structure. Fig. 3 indicates that χ rapidly decreases below about 35 K with decreasing temperature, and shows a slight upturn below 12 K. These results are consistent with the result of single crystal and powder sample reported by Ueda and co-workers[11, 20]. In Fig. 3 the upturn of χ below 12 K is considered to be due to the existence of impurities and/or free ions caused by defects. The rapid reduction of the spin susceptibility below 35 K strongly suggests the existence of a spin-Peierls transition. It is worth pointing out that all the samples prepared under different pH values show a spin-Peierls transition. This suggests that the NaV_2O_5 with spin-Peierls transition has been successfully synthesized by hydrothermal synthesis. It should be pointed out that NaV_2O_5 is not an ordinary spin-Peierls transition but an exotic transition accompanying spin gap and charge ordering. It is different from the inorganic spin-Peierls compound $CuGeO_3$, for which the driven BCS-type formula $2\Delta/k_BT_{sp} = 3.53$ holds well, where Δ is a spin-gap energy at $T = 0$ K[21]. While such a measurement is 6. 44 for NaV_2O_5[6]. Although we pay our special attention to 1D-quantum size

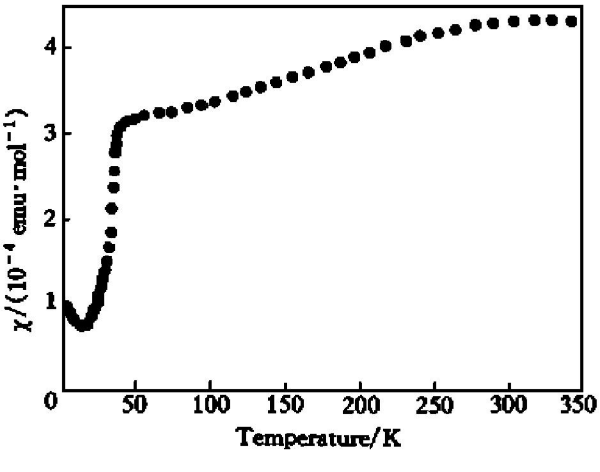

Fig. 3 Temperature dependence of magnetic susceptibility of sample NaV_2O_5 prepared under pH value of 8. 3 at $H = 1$ T

effect of magnetism of nanorods of NaV_2O_5, yet it has not been observed and they show identical magnetic properties as their bulk counterparts. This is due to their relatively large diameter of as-prepared nanorods.

4 CONCLUSIONS

We have successfully synthesized 1D NaV_2O_5 nanorods by a direct hydrothermal synthesis at relatively low temperature. Alkaline conditions are more favored in present study unlike previous methods. Hydroxylamine hydrochloride, the reducing agent, may play a key role in the growth of rod-like products. The nature of final products can be chemically controlled by the factors of pH value, reductants etc. The vanadium oxide nanorods open up fascinating possibilities for further chemical and physical explorations of nanostructures and hold promise for possible applications.

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