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Structures and magnetic anisotropy of β-$Mn_2V_2O_7$ crystals synthesized by the molten salt method

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β-$Mn_2V_2O_7$ crystals with strip shape are successfully prepared by the molten salt method in a closed crucible, and are characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area of electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). The results indicate that the sample is of the β-$Mn_2V_2O_7$ crystal with monoclinic symmetry, level natural cleavage facets and directional growth. Magnetic properties are measured by vibration sample magnetometry (VSM) at room temperature, and the magnetic hysteresis loop indicates that the β-$Mn_2V_2O_7$ has anti-ferromagnetic properties with low coercive force and remnant magnetization. The magnetic measurement results in different directions exhibit that the β-$Mn_2V_2O_7$ has magnetic anisotropy, which is due to the fact that the magnetic interaction energy of the β-$Mn_2V_2O_7$ is lowest only when the electron configuration is in a certain direction.

Keywords: β-$Mn_2V_2O_7$, molten salt synthesis, magnetic anisotropy
PACC: 7550E, 7530G, 6125K

1. Introduction

The low-dimensional magnetic materials $M_2V_2O_7$ (M=Cu, Mn, Co, Ni) have aroused much interest in solid state chemistry and physics due to their abnormal behaviour and subsequent desirable properties which mainly deal with electrical and magnetic properties.[1−3] These may be ascribed to their high-specific capacity and layered crystal structure; in particular, the honeycomb structure is of great interest.[4] $Mn_2V_2O_7$ is found to have a peculiar distorted honeycomb structure, which exhibits two phases of a high-temperature form (β-form) and a low-temperature form (α-form): the β-form crystallizes in the monoclinic system of space group $C2/m$ with $a = 0.67129(6)$ nm, $b = 0.87245(5)$ nm, $c = 0.49693(4)$ nm, and $\beta = 103.591(8)^\circ$ while the α-form crystallizes in the triclinic system of space group $P\bar{1}$ with $a = 0.6868(2)$ nm, $b = 0.7976(2)$ nm, $c = 0.10927(2)$ nm, $\alpha = 87.81(1)^\circ$, $\beta = 72.14(1)^\circ$, and $\gamma = 83.08(1)^\circ$.[5] One of the most significant differences in structural feature between the α and β forms is that the honeycomb layers in the β-form are parallel to the (001) plane and those in the α-form are parallel to the (110) plane. The crystallographic phase transition between the α-forms and the β-forms is suggested to occur below 300K, indicating that only the β-form can be crystallized at high temperatures.[6]

Up to now, there have been only a few reports of syntheses and properties of $Mn_2V_2O_7$. Liao *et al* [5] studied hydrothermal synthesis and magnetic properties of single crystal $Mn_2V_2O_7$. He and Ueda[7−9] investigated flux growth, magnetic properties and martensitic-like transition of single crystal $Mn_2V_2O_7$ in detail. Liu and Zeng[10] reported hydrothermal synthesis of β-$Mn_2V_2O_7$ microtubes and hollow microspheres. A number of synthetic methods have been developed to prepare vanadates with various sizes and morphologies.[5,10] These methods are often restricted by the requirements for high temperature, special conditions, tedious procedures and protective atmosphere sintering. Therefore, practical methods of preparing large scale vanadates at low cost are still a great challenge for present and future studies. The molten salt method is a recently developed method to prepare inorganic material powders, and it has some unique features compared with the solid method, co-precipitation and sol–gel and hydrothermal methods of powder synthesis. Compared with any other synthesis means, the molten salt method has some advantages, i.e. lower reaction temperature, less reaction time, high-purity product, and anisotropic growth of product.[11] As chemical reaction media, molten salt provides a fine chemical reaction environment where grains have an anisotropic growth rate.

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So, the molten salt method is widely used for the synthesis of anisotropic growth powders and special morphology powders.

In this paper, strips of β-$Mn_2V_2O_7$ crystals are successfully prepared by the molten salt method. Compared with the other route in Ref.[9], the new route in this paper uses a lower temperature, less reaction time and different solvents. Then the structure and the magnetic anisotropy of the β-$Mn_2V_2O_7$ were studied by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area of electron diffraction and vibration sample magnetometry (VSM) at room temperature. Furthermore, the correlations between anisotropic structures of polycrystalline product and magnetic anisotropy are first reported.

2. Experimental

Inorganic chloride salt is a considerable flux material for the growth of complex metal oxides due to its low melting point and low price. Also, the $Mn_2V_2O_7$ compound was prepared by the molten salt method from mixtures of V_2O_5, $MnSO_4.H_2O$, KCl, $MnCl_2$ in air. A powder mixture of V_2O_5 and $MnSO_4.H_2O$ was used as a reactant. An inorganic salt mixture was prepared using KCl and $MnCl_2$ (purity higher than 99.0 wt %) with KCl content of 50 mol% as a solvent. The starting materials were ground together and packed into a closed alumina crucible. Then these materials were heated in different steps at 300 and 600 °C. Each thermal treatment lasted 24 hours and was preceded by regrinding the sample to homogenize the reaction products. A final thermal treatment was performed at 900°and kept at 900 °C for 3–5 hours to ensure that the solution melts were completely homogeneous. The furnace was cooled down to room temperature at a rate of about 100 °C/h. Finally, β-$Mn_2V_2O_7$ crystals with strip shape were obtained by mechanical separation from the surface of the melt salt.

The XRD pattern of the sample was collected at room temperature in a 2θ range from 10 to 90° with a step of 0.02° and a fixed counting time of 4 s using an X' Pert PRO MPD XRD system with Cu Kα radiation, a voltage of 40 kV and a current of 40 mA. The morphology of the sample surface and the concentration of element content were measured on an FEI-SIRION SEM. Transmission electron microscope (TEM) micrographs and selected-area electron diffraction patterns were obtained on a PHILIPS-CM200 and JEM-2010 type TEM. Magnetic measurements were performed on a Lake shore-VSM 7410A at room temperature.

3. Results and discussion

3.1. Structure characterization

Figure 1 shows the x-ray powder diffraction pattern of the sample with strip shape. It is found that these peaks can readily be indexed with monoclinic symmetry, and the diffraction peaks of the β-$Mn_2V_2O_7$ (PCPDF NO. 73-1806) may be identified.

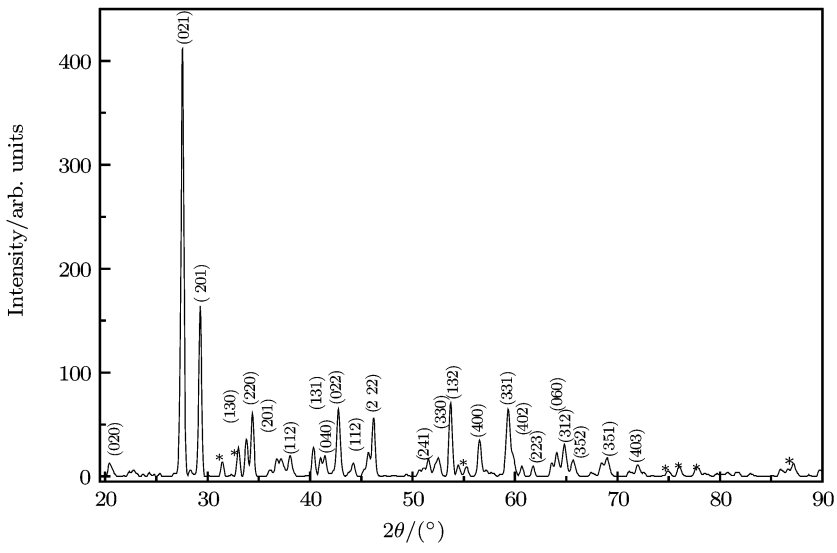


Fig.1. X-ray diffraction pattern of the β-$Mn_2V_2O_7$ powder.

Minor peaks of impurity phases are present in Fig.1 (shown by asterisks). All the peaks of impurity phases almost accord with the XRD patterns of manifold oxides. Hence, it is difficult to index the peaks of impurity phases.

According to monoclinic symmetry, the lattice constant can be calculated from the following formula:

$$d = \frac{1}{\sqrt{\frac{\left(\frac{h}{a}\right)^2 + \left(\frac{l}{c}\right)^2 + \frac{2hl\cos\beta}{ac}}{\sin\beta} + \left(\frac{k}{b}\right)^2}}, \qquad (1)$$

where d is the interplanar distance, h, k, l are crystal plane indexes, a, b, c, β are the cell parameters. Cell parameter values can be calculated to be $a = 0.67354$ nm, $b = 0.81086$ nm, $c = 0.48975$ nm and $\beta = 103.568°$. These data are close to those given by Liao *et al.*[5] It can be considered that the observed differences are caused by the slight change in oxygen content.

According to XRD pattern data, average grain size is approximately calculated by means of the Scherrer formula,

$$D = K\lambda/\beta\cos\theta, \qquad (2)$$

where D is the grain size in the direction perpendicular to the crystal plane, K is a constant of 0.89, λ is the x-ray wavelength (0.15406 nm), β is the half width of the peak, θ is the diffraction angle, and the grain size of the calculated result is 17.97 nm.

3.2. Morphology of the sample

Figure 2 shows a macroscopic picture of the β-$Mn_2V_2O_7$ crystal with a strip-like shape taken by a digital camera. From Fig.2, one can see that the length of the β-$Mn_2V_2O_7$ is about 10–50 mm.

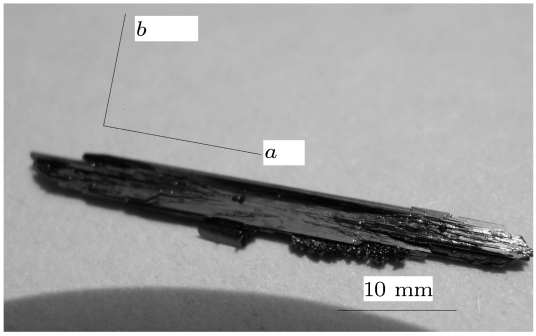


Fig.2. Macroscopic shape of the β-$Mn_2V_2O_7$ crystal obtained by the molten salt method.

A scanning electron microscopic image (Fig.3) shows that the morphology of the β-$Mn_2V_2O_7$ has a strip shape with horizontal natural cleavage facets. Moreover, the β-$Mn_2V_2O_7$is grown in a given direction. This indicates that β-$Mn_2V_2O_7$ crystals are easy to diffuse in some direction in molten salt. Figure 4(a) shows a low-resolution TEM image of β-$Mn_2V_2O_7$, which further demonstrates that the obtained sample has a uniform strip-like morphology. Figure 4(c), the HRTEM image taken from the single strip, shows clearly resolved lattice fringes and an interplanar spacing measured to be 0.522 nm. The crystal face corresponds to the (110) plane of the β-$Mn_2V_2O_7$. The lattice fringes in Fig.4(c) show the crystalline integrality of the sample. The SAED pattern (Fig.4(b)) of β-$Mn_2V_2O_7$ is easily indexed on the basis of a monoclinic cell, which is in good agreement with the XRD pattern data. All these further prove that the strip is crystals with directional growth and crystalline integrality.

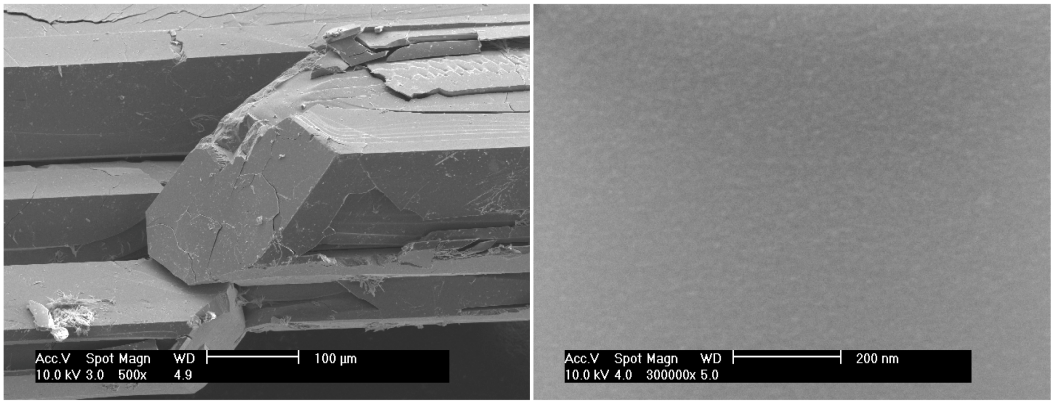


Fig.3. SEM image of the β-$Mn_2V_2O_7$ synthesized by the molten salt method.

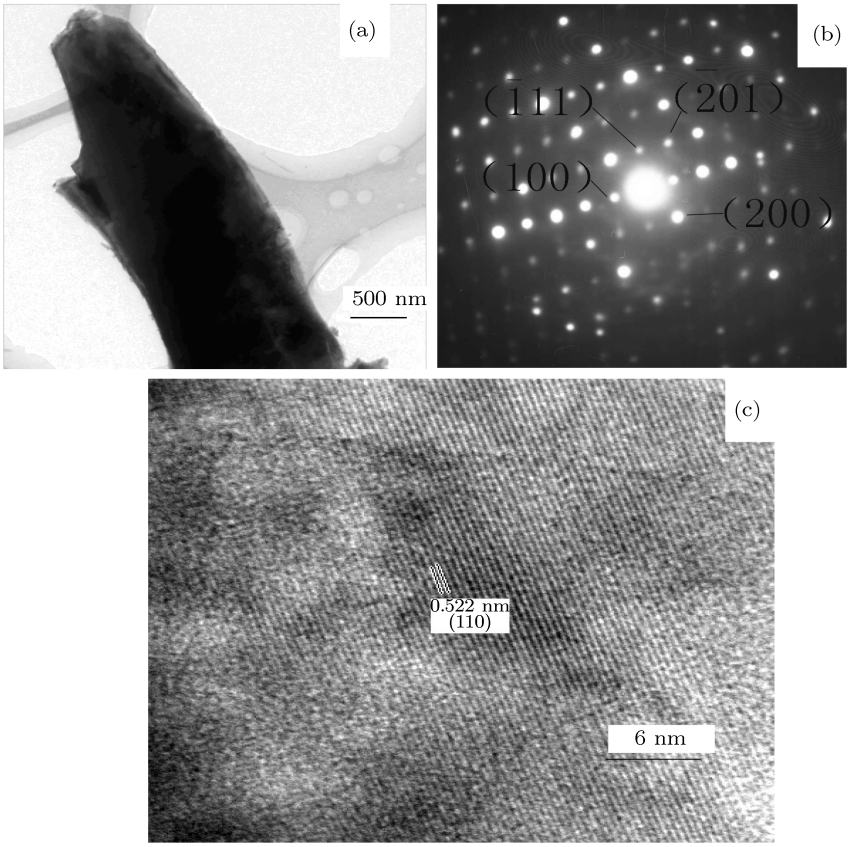


Fig.4. TEM image (a), SAED pattern (b), HRTEM image (c) of the β-$Mn_2V_2O_7$ synthesized by the molten salt method.

In addition, the EDX spectrum of the β-$Mn_2V_2O_7$ crystal confirms that no other metal elements except for Mn and V were detected. The molar ratio of Mn:V:O is calculated to be approximately 2:2:7, and this is consistent with that of the formula of $Mn_2V_2O_7$.

3.3. Magnetic properties

The magnetization M as a function of applied field H at room temperature is shown in Fig.5. Clear hysteresis and remnant magnetization indicate that the β-$Mn_2V_2O_7$ crystals with strip shape are antiferromagnetic. Figure 5 further shows that the coercive force and the remnant magnetization are very low. Linear behaviour of the magnetization is observed above 0.5 T and no magnetization saturation is found above 1 T. The magnetization along the b direction is 3–5 times as large as that along the a direction in the $a-b$ plane at room temperature. These results indicate the presence of magnetic anisotropy and antiferromagnetic (AF) ordered ground state. The magnetic anisotropy accords with the anisotropic growth shown in the SEM and TEM patterns. According to the theory of Akulov[12,13] magnetic crystal anisotropy originates from magnetic interaction of the spin magnetic moment, and the classic energy of the magnetic interaction is described by the following formula:

$$E = g^2\mu_B^2 \sum \left[\frac{s_i s_j}{r_{ij}^3} - \frac{3(s_i r_{ij})(s_j r_{ij})}{r_{ij}^5}\right], \qquad (3)$$

where g is the electronic magnetic force ratio, $g = 2$; μ is the Bohr magneton; r_{ij} is the vector diameter of electron i and electron j; Σ is the summation of all paired electrons in the crystal.

For a certain shape of ferromagnetic crystal, the energy of magnetic interaction is actually the actions of the demagnetizing field and Lorentz field. The demagnetizing field is related to crystal shape, and the Lorentz field is related to crystal structure. Furthermore, the magnetic anisotropy of the β-$Mn_2V_2O_7$ is responsible for directional growth, which is observed in the SEM and TEM measurements. According to the theory of single-ion anisotropy, magnetic crystal

anisotropy of the β-$Mn_2V_2O_7$ affects the crystal field. When the non-full shell electron configuration with respect to the crystal axis is in different directions in Mn^{2+} ion, the energy of magnetic interaction is different. Only when the electron configuration is in a certain direction, will its energy be lowest. By means of spin–orbit coupling, magnetic intensities in different directions are related to crystal free energy. Therefore, the magnetic anisotropy of the β-$Mn_2V_2O_7$ may be caused by crystal free energy of spin–orbit coupling in the Mn^{2+} ion, while He and Ueda[8] proposed that Mn^{2+} ions had a high spin state and β-$Mn_2V_2O_7$ exhibited magnetic anisotropy due to admixture of the orbital moments.

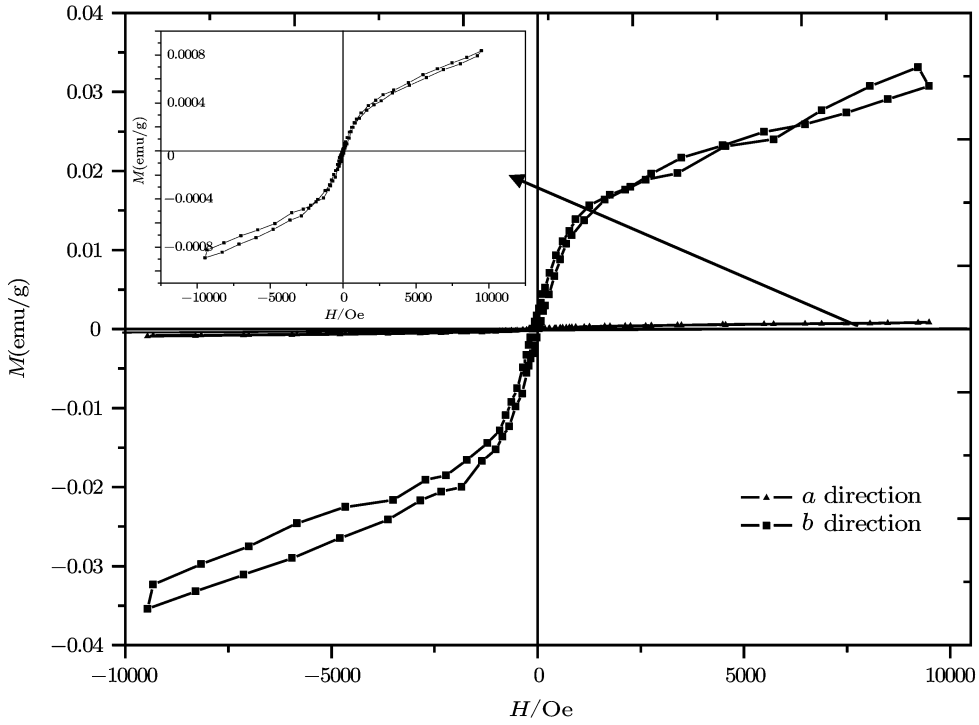


Fig.5. Magnetization M as a function of the applied field H at room temperature along directions perpendicular and parallel to the length of the strip in a plane. The inset shows the magnetization function of H along the direction of a (parallel to the length of the strip in a plane). The direction of a is parallel to the length of the strip, the direction of b is perpendicular to the length of the strip (1 Oe=79.5775 A/m).

4. Conclusions

Manganese (II) divanadate $Mn_2V_2O_7$ with strip shape has been synthesized by the molten salt method. XRD and SAED patterns show that the sample is of β-$Mn_2V_2O_7$ with monoclinic symmetry. SEM and TEM images show that the shape of the β-$Mn_2V_2O_7$ has horizontal natural cleavage facets. These results indicate that the strip is a crystal with directional growth and crystalline integrality. The magnetic hysteresis loop indicates that the β-$Mn_2V_2O_7$ is anti-ferromagnetic with low coercive force and remnant magnetization at room temperature. The results of studying magnetic properties in different directions indicate that the magnetization along a direction perpendicular to the length of the strip in a plane is much more than that along a direction parallel to the length of the strip in a plane at room temperature. The reason why the magnetic anisotropy of the β-$Mn_2V_2O_7$ crystal is existent is because the energy of magnetic interaction is lowest only when the electron configuration is in a certain direction. Magnetizations in different directions are related to crystal free energy through spin–orbit coupling.

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