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Molten salt synthesis and characterization of large size β-$Mn_2V_2O_7$ with single crystal character

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ABSTRACT

The β-$Mn_2V_2O_7$ crystals with strip-like shape were successfully synthesized by molten salt method in different molten salt. The samples were investigated by XRD, SEM, TEM, HRTEM and SAED. The results show molten salt species, molten salt content and heating temperature have great effect on the crystal structure and morphology. The products were found to have a monoclinic structure and possess a uniform strip-like shape with different grain size. The XRD patterns and the SAED patterns of single strip indicate that the β-$Mn_2V_2O_7$ single strip have single crystalline character. HRTEM image further substantiate that the β-$Mn_2V_2O_7$ strip have anisotropy growth and crystalline integrality.

1. Introduction

In recent years, transition metal vanadates materials have been inclusively researched on its electrical, magnetic and optical properties [1–5]. As a kind of low-dimensional magnetic materials, $Mn_2V_2O_7$ has been receiving more and more attention in solid-state chemistry and physics [6–8]. These fantastic magnetic properties may be due to their layered crystal structure [9]. $Mn_2V_2O_7$ is found to have a peculiar distorted honeycomb structure, which exhibits a high-temperature form (β-form) and a low-temperature form (α-form). Its crystallographic phase transition between α-forms and β-forms is suggested to occur below 300 K, indicating that only β-form can be crystallized at high temperature [9]. Fig. 1 shows the thortveitite structure of β-$Mn_2V_2O_7$, which consists of crystallographic V and Mn site. The structure can be described as a close hexagonal packing of the oxygens with Mn^{2+} cations in octahedral holes and vanadium in tetrahedral holes in alternating parallel layers (0 0 1). It can be seen that the honeycomb layers in the β-form are parallel to the (0 0 1) plane. It is composed of edge-sharing MnO_6 octahedra, forming $(MnO_3)_n$ layers connected together by V_2O_7 divanadate groups situated on both sides of honeycomb-like cavities. All of the oxygen atoms in the $(MnO_3)_n$ layers are shared with V_2O_7 groups, which adopt a staggered conformation with a linear V–O–V moiety [6,10,11].

The special structure exhibits that different type of cations can be distributed and ordered in layered structure consist of octahedral and tetrahedral sites. This capability for metal accommodation opens a possibility of tuning some properties through morphology control. A lot of synthetic means have been developed to prepare vanadates with various morphologies [12–16]. He and Ueda [8,13] investigated flux growth synthesis and martensitic-like transition of single crystal $Mn_2V_2O_7$ in detail. Liu and Zeng [12] reported hydrothermal synthesis of β-$Mn_2V_2O_7$ microtubes and hollow microspheres. Among various synthesis means, molten salt synthesis is a kind of advanced and old synthesis method which possesses some advantage such as lower reaction temperature and less reaction time, higher purity of product, anisotropic growth of product. As chemical reaction mediums, molten salt provides a fine chemical reaction environment where grains have anisotropic growth velocity. So, molten salt method is widely used for the synthesis of anisotropic growth powders and special morphology powders. However, up to now, no papers on molten salt synthesis of β-$Mn_2V_2O_7$ have been reported. In this study, a novel and simple

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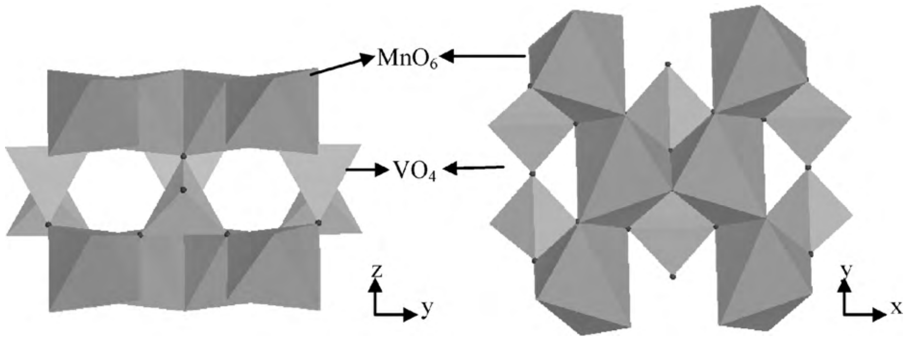

Fig. 1. Crystal structure of thortveitite β-$Mn_2V_2O_7$. Dark grey octahedron: MnO_6; French grey tetrahedral: VO_4; Black sphere: O ion.

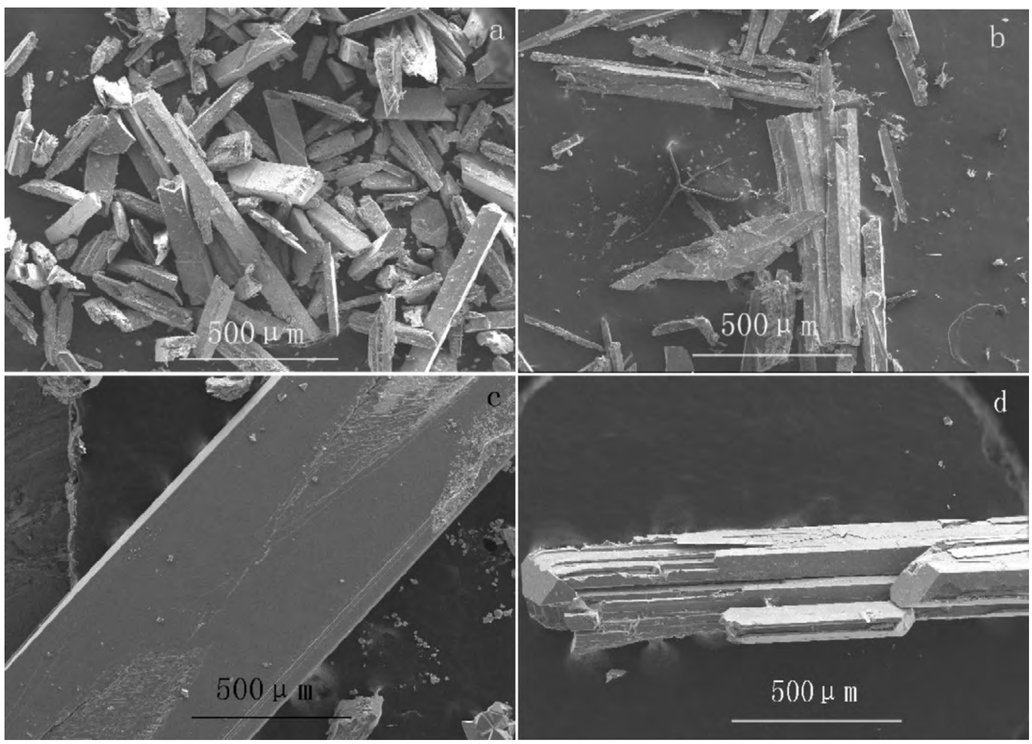

Fig. 2. SEM images of the as-synthesized β-$Mn_2V_2O_7$ in different molten salts. (a) Reactants ($MnSO_4$ + V_2O_5) + molten salt (LiCl + KCl); (b) Reactants ($MnSO_4$ + V_2O_5) + molten salt (LiCl + $MnCl_2$); (c) Reactants ($MnSO_4$ + V_2O_5) + molten salt (KCl + $MnCl_2$); (d) Reactants ($MnSO_4$ + V_2O_5) + molten salt (NaCl + $MnCl_2$).

molten salt method was successfully developed to prepare large size β-$Mn_2V_2O_7$ crystal with single crystal character. The effect of different process parameters on the structure and morphology of the β-$Mn_2V_2O_7$ crystals will be discussed. Anisotropy structure of bulk crystal with single crystal character was studied in detail.

2. Experimental

The β-$Mn_2V_2O_7$ was prepared by direct molten salt synthesis using appropriate amount of V_2O_5, $MnSO_4.H_2O$, NaCl, LiCl, KCl, $MnCl_2$. All raw materials with analytical grade were purchased from Beijing Chemical Reagents Company and used without further purification. Certain mixtures of LiCl, KCl, NaCl and $MnCl_2$ play an important role to afford a molten salt liquid at high temperature because of its low melting temperature. V_2O_5 and $MnSO_4{\cdot}H_2O$ as reactants and different molten salts were mixed in a desired mole ratio by ball milling with zirconia balls as grinding media in ethanol for 24 h. Then these materials were heated in different steps at 300 and 600 °C. Each thermal treatment lasts for 24 h and was preceded by regrinding the sample to homogenize the reaction products. A final thermal treatment is performed at 900 °C and kept for 3–5 h in a closed crucible to ensure that the solution melts completely and homogeneously. The furnace was cooled down to room temperature at a rate of about 100 °C/h. At last, large size β-$Mn_2V_2O_7$ crystals with strip shape were obtained by means of soaking and washing the products.

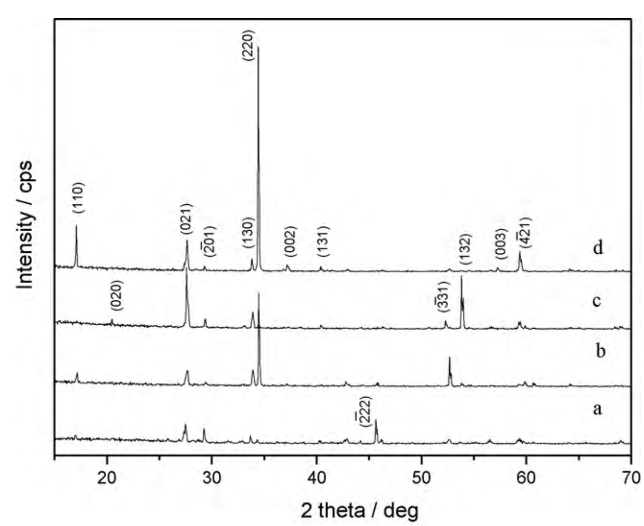

Fig. 3. XRD patterns of the as-synthesized β-$Mn_2V_2O_7$ in different molten salts.

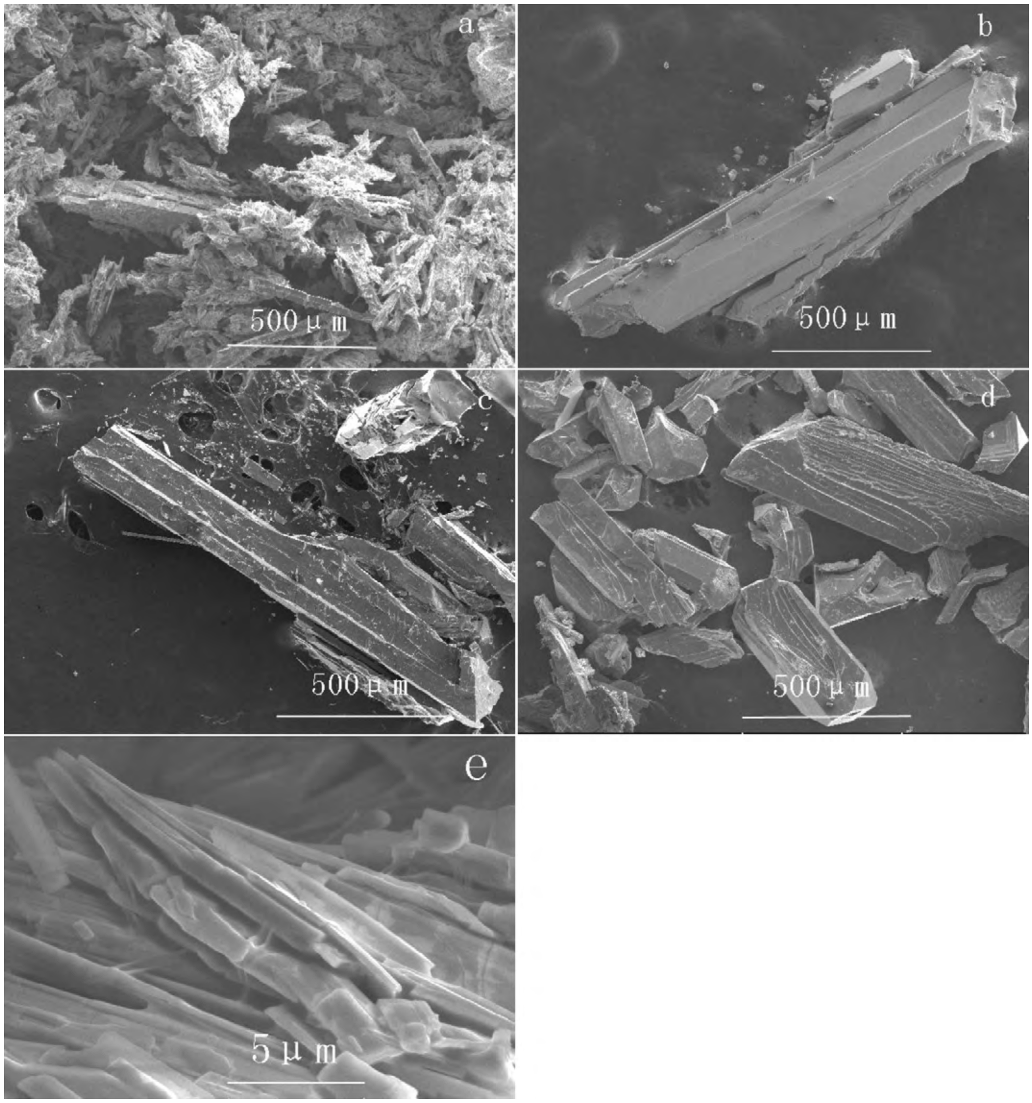

Fig. 4. SEM images of the as-synthesized samples in different molten salt mass. (a) R = 1.5; (b) R = 3; (c) R = 4; (d) R = 5; (e) High magnified pattern of (a). R ($M_{salts}/M_{reactants}$) is the mass ratio of molten salt and the reactants.

The X-ray diffraction (XRD) pattern of the samples were collected at room temperature in the 2θ range from 10° to 90° with a step width of 0.02° and a fixed counting time of 4 s using a X′Pert pro MPD X-ray diffraction (XRD) system with Cu Kα radiation, a voltage of 40 kV and a current of 40 mA. The morphology of the sample surface were observed by scanning electron microscopy (SEM) image and the concentration of element content was measured by energy dispersive spectrometer (EDS), taken with a FEI-SIRION scanning electronic microanalyzer. The transmission electron microscope (TEM) micrographs, high-resolution transmission electron microscopy (HRTEM) and select area electronic diffraction pattern (SAED) were obtained on PHILIPS-CM200 and JEM-2010 type TEM.

3. Results and discussion

3.1. Effects of molten salt species on the β-$Mn_2V_2O_7$ structure and morphology

The mixture of different molten salt and reactants was heated at 900 °C for 3 h to prepare β-$Mn_2V_2O_7$, which is shown as follows:

(a) Reactants ($MnSO_4$ + V_2O_5) + molten salt (LiCl–KCl);
(b) Reactants ($MnSO_4$ + V_2O_5) + molten salt (LiCl–$MnCl_2$);
(c) Reactants ($MnSO_4$ + V_2O_5) + molten salt (KCl–$MnCl_2$);
(d) Reactants ($MnSO_4$ + V_2O_5) + molten salt (NaCl–$MnCl_2$).

Fig. 2 shows the SEM patterns of the samples obtained at 900 °C in different molten salts. The samples exhibit exclusively long strip shape with the length of from several hundreds micrometers to several millimeters and the width of 100–600 μm. The products synthesized in LiCl–KCl possess minimal grain size while possess maximum grain size in $MnCl_2$–KCl. The samples prepared in LiCl–KCl have a long tetragonal prism shape with both the width and the height of about 100 μm. The samples prepared in LiCl–$MnCl_2$ have a greater tetragonal prism with nonuniform grain size. However, the shape of the samples prepared in $MnCl_2$–KCl is a long batten with the width of about 800 μm and the height of about 100 μm. The shape of the samples prepared in $MnCl_2$–NaCl is a regular polyhedron with layer cleavage plane. The height of these crystals has little difference, however, the width has an obviously change. The results reveal that these crystals have a remarkable anisotropic growth. Fig. 3 shows the XRD patterns of the samples prepared in different molten salts. The calculated d-spacing and relative intensity are listed in Table 1. The results show that all as-synthesized samples are composed of monoclinic system $Mn_2V_2O_7$. The crystallinity of the samples increases gradually from sample a to sample d. Therefore, mixed salt $MnCl_2$–NaCl were served as medium molten salt for preparing β-$Mn_2V_2O_7$. In addi-

Table 1
Powder diffraction data on β-$Mn_2V_2O_7$ prepared in different molten salts.

h k l	Sample a		Sample b		Sample c		Sample d	
	d (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*	*d* (nm)	*I*
1 1 0	0.5216	20	0.5174	11	–	–	0.5189	13
0 2 1	0.3246	100	0.3226	25	0.3225	100	0.3226	12
−2 0 1	0.3048	60	0.3033	6	0.3039	17	0.3045	12
1 3 0	0.2656	26	0.264	25	0.2642	30	0.2647	4
2 2 0	0.2609	20	0.26	100	0.2602	8	0.2601	100
3 3 0	0.1738	28	0.1735	34	–	–	0.1736	1
−4 2 1	0.1556	30	0.1545	9	0.1555	17	0.1554	7

tion, it is noted that the XRD pattern of sample c has an obvious difference compared with the other XRD patterns. The discrepancy shows that the samples prepared in different molten salt have different anisotropic growth direction. Different viscosity of molten salts and different solubility of reactants in molten salts have great effect on the reaction process, the crystal shape and grain size. These results reveal that the reactants in molten salt $MnCl_2$–KCl have larger solubility and larger degree of supersaturation, lower viscosity than in others molten salt. The chloride ions have a great interaction with closed-packed face, and that limit growth rate in some directions, which lead to anisotropic growth.

3.2. Effects of molten salt content on β-$Mn_2V_2O_7$ structure and morphology

To study the effect of molten salt content on the formation of β-$Mn_2V_2O_7$, the samples were prepared at 900 °C by using different molten salts content. The mass ratio of molten salts ($MnCl_2$–NaCl) to reactants ($MnSO_4$ + V_2O_5) is 1.5, 3, 4, 5, respectively. SEM images, shown in Fig. 4., indicate that all samples have a similar strip-like shape. The samples synthe-

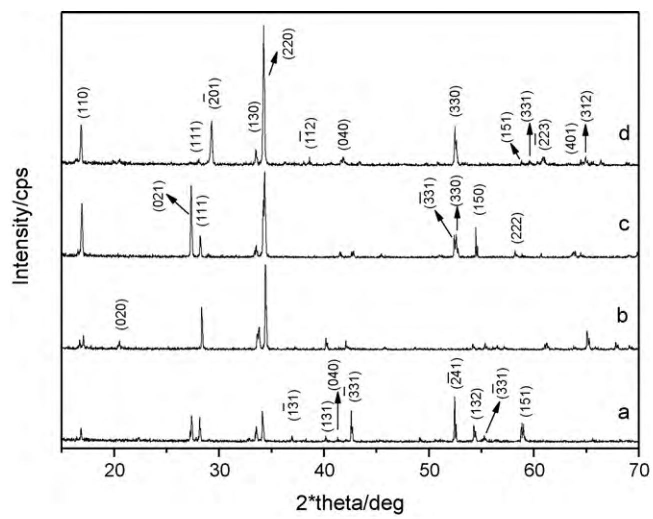

Fig. 5. XRD patterns of the as-synthesized samples in different molten salts mass. (a) R = 1.5; (b) R = 3; (c) R = 4; (d) R = 5; R ($M_{salts}/M_{reactants}$) is the ratio of molten salt mass and the reactants mass.

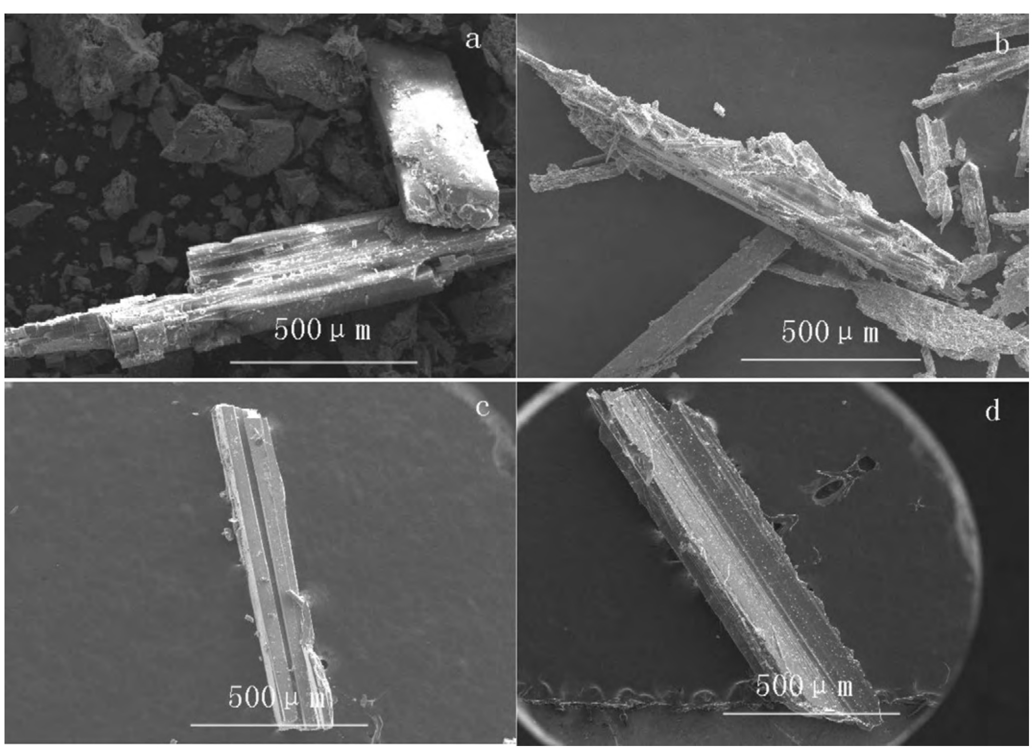

Fig. 6. SEM images of the samples prepared by molten salt method at different heat treatment temperature. (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1000 °C.

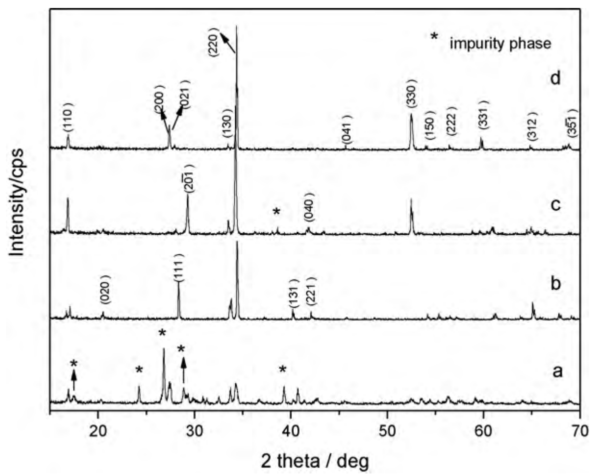

Fig. 7. XRD patterns of the samples prepared by molten salt method at different heat treatment temperature. (a) 700 °C; (b) 800 °C; (c) 1000 °C; (d) 900 °C.

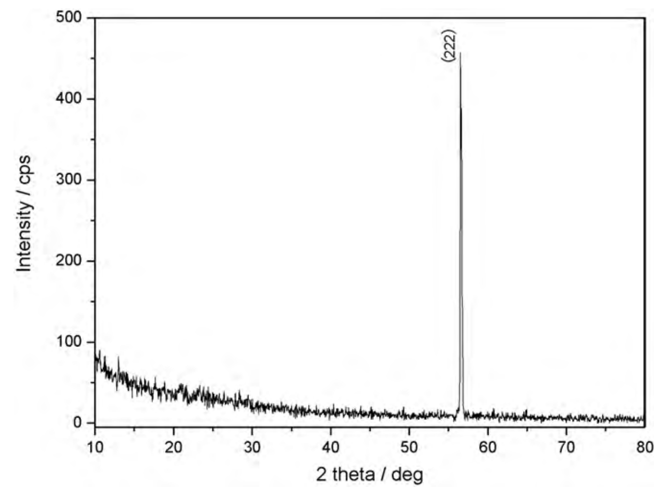

Fig. 9. XRD pattern along surface a–b of β-$Mn_2V_2O_7$ single strip.

sized when $M_{salts}/M_{reactants}$ = 1.5 have a long strip shape and the particles with nonuniform size agglomerate together. With the increase of molten salt content, the regularity degree is also gradually enhanced and the grain size increases at first and then decreases. The XRD pattern, shown in Fig. 5., indicates the samples prepared by using different molten salts content are single phase (monoclinic system β-$Mn_2V_2O_7$). The crystallinity of the samples is improved at first and then declines with the increase of molten salts content. The results show that the reactions may be incomplete if molten salts content are deficient and reaction efficiency may be reduced if salts mass are excessive.

3.3. Effects of heating temperature on β-$Mn_2V_2O_7$ structure and morphology

Mixture of reactant and molten salt $MnCl_2$–NaCl were heated at different heating temperature (700, 800, 900, 1000 °C) for 3 h. The SEM images, which are shown in Fig. 6, indicate all samples possess long strip shape. With the increase of heating temperature, the particle size also increases and the crystal smoothness is enhanced. The XRD patterns in Fig. 7 show that the samples heated at 700 °C contain some impurity phase and monoclinic $Mn_2V_2O_7$ phase, indicating the reactions are incomplete at 700 °C. As the temperature is raised up to 800 °C, $Mn_2V_2O_7$ phase is formed completely. The crystallinity was enhanced with increasing heating temperature. However, the purity of the samples prepared at 1000 °C is lower than that at 900 °C, which may be induced by small quantity of salts infiltrating into the samples at exorbitant heating temperature. The results show that the heating temperature plays an important role for the formation of β-$Mn_2V_2O_7$ crystal.

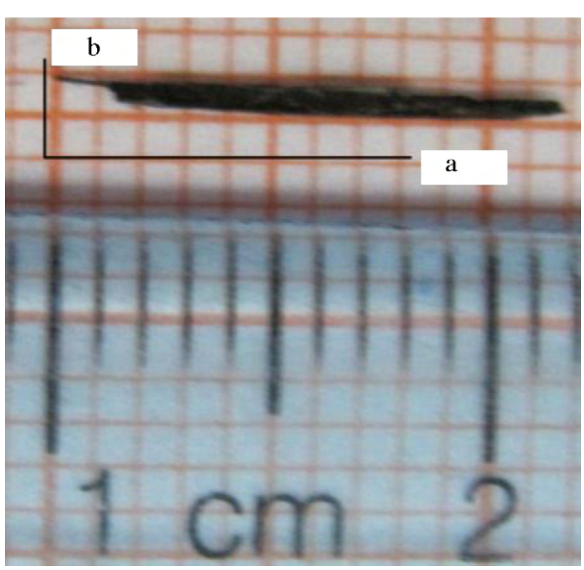

Fig. 8. Macroscopic photograph of the β-$Mn_2V_2O_7$ single strip crystal prepared in molten salt $MnCl_2$ + NaCl at 900 °C.

3.4. Anisotropy structure analysis

Fig. 8 shows the macroscopic picture of β-$Mn_2V_2O_7$ single strip, which is taken by digital camera. It can be seen in Fig. 8 that the β-$Mn_2V_2O_7$ strip has a length of about 12 mm and a width of about 0.5 mm. Fig. 9 indicates the XRD pattern along surface a–b of single strip crystal prepared in molten salt $MnCl_2$–NaCl. The X-ray powder diffraction pattern of the same sample is shown in Fig. 7(d). The results indicate the phase of the strip crystal is in accordance with JCPDF card No. 73-1806, which is β-$Mn_2V_2O_7$ phase with monoclinic system. The crystal anisotropy growth is obvious, especially in the direction of plane (2 2 2). It also show a–b crystal plane is (2 2 2).

The TEM images (Fig. 10(a)) demonstrate that the obtained sample has a uniform layer structure. The SAED pattern (Fig. 10(b)) of the as-obtained β-$Mn_2V_2O_7$ is yet corresponding to the monoclinic phase (JCPDF), which shows single crystal character. The HRTEM image (Fig. 10(c)), which is taken from the layer crystal, shows the β-$Mn_2V_2O_7$ crystal has clearly resolved lattice fringes and the inter-planar spacing was measured as 0.306 and 0.436 nm, which corresponds to two intersecting plane of the ($\bar{2}$ 0 1) plane and the (0 2 0) plane, respectively. And that it can be inferred that the incident electronic direction (the intersecting line of two planes) is along crystal orientation [1 0 2] and the plane in TEM patterns (Fig. 10(a)) is (2 0 3). All these results further substantiate that the β-$Mn_2V_2O_7$ strip have anisotropy growth and crystalline integrality.

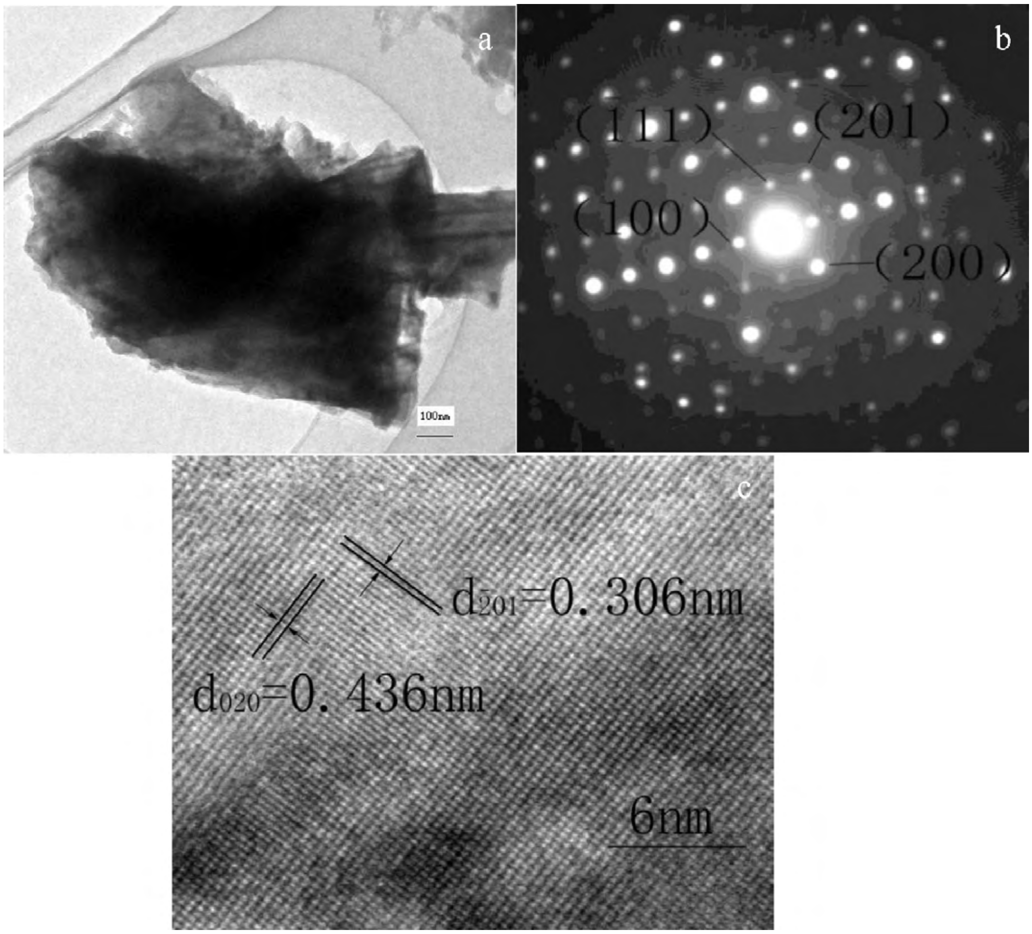

Fig. 10. TEM image (a), SAED pattern (b), HRTEM image (c) of β-$Mn_2V_2O_7$ prepared by molten salt method.

4. Conclusions

In this paper, we introduced a kind of novel molten salt synthesis technique in different inorganic chloride salt at 900 °C to fabricate large size β-$Mn_2V_2O_7$ crystal. The samples exhibit exclusively long strip shape with a length of from several hundreds micrometers to several millimeters. All samples are composed of monoclinic structure β-$Mn_2V_2O_7$. The crystallinity of the product prepared in $MnCl_2$–NaCl is the best in all molten salt species. With increasing molten salt content, the crystal regularity degree is also gradually enhanced, while the crystallinity and grain size of the samples increase at first and then decrease. The crystallinity is enhanced with the increase of heating temperature. Therefore, the optimum condition of molten salt synthesis of β-$Mn_2V_2O_7$ is the heating temperature of 900 °C, $M_{salts}/M_{reactants} = 4$, $MnCl_2$–NaCl serving as molten salt. Thus, molten salt species, molten salt content and heating temperature have great effect on crystal structure, morphology and grain size. The XRD pattern and SAED patterns of the single strip indicate β-$Mn_2V_2O_7$ single strip have single crystal character. HRTEM and SAED further substantiate β-$Mn_2V_2O_7$ with strip shape have anisotropy growth and crystalline integrality.

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