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LETTER

Preparation and characterization of $ZrWMoO_8$ powders with different morphologies using hydrothermal method

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Materials that exhibit negative thermal expansion (NTE) property are of considerable scientific and technological interests [1–5]. Their use in composites facilitates the control of bulk thermal expansion properties to avoid cracks or separation at interfaces between the two components, which is especially needed for various applications in optics, electronics, and other fields where exact positioning of parts is crucial [6, 7]. For use in composite, an ideal NTE material should have isotropic and linear negative thermal expansion properties during a large temperature range including room temperature [8]. It is desirable that the material is thermodynamically stable over its NTE range and can be prepared in a low-cost and efficient way.

The most promising NTE material to date is ZrW_2O_8 family due to its' isotropic NTE property over a wide temperature range. The typical material, ZrW_2O_8, undergoes isotropic NTE behavior from 0.3 K to 1050 K [9,10]. Unfortunately, for use in composites, there are some drawbacks. For example, ZrW_2O_8 undergoes an order-disorder phase transition around 430 K and the linear coefficient changed from $-8.8 \times 10^{-6}\ K^{-1}$ to $-4.9 \times 10^{-6}\ K^{-1}$[11]. It also undergoes a phase transition to a more dense structure (with a significantly lower coefficient of NTE) at around 0.2 Gpa. While structurally related phases such as $ZrMo_2O_8$ and $ZrW_{2-x}Mo_xO_8$ solid solution do not undergo phase transition over the NTE temperature range, which makes it desirable in preparing composite materials [12–14].

Cubic $ZrWMoO_8$ is a typical $ZrW_{2-x}Mo_xO_8$ solid solution. But it is difficult to prepare due to the volatilization of WO_3 and MoO_3 when conventional solid state techniques is used. The breakthrough in this area came when dehydration of the precursor method was put forward [15]. But this method was far from optimal because the solution usually was aged and gelatinized for weeks. Recently, a rapid synthetic route, hydrothermal method was approached and highly crystallized cubic $ZrWMoO_8$ powders were achieved without the aging procedure [16]. As used as fillers in composites, for decreasing the innerstress, proper morphology is important. But to date, most NTE materials have been synthesized as powders without controlling in morphology due to the difficulty in synthesis.

In this paper, $ZrWMoO_8$ powders with different morphologies were prepared by hydrothermal method using HCl, $HClO_4$, HNO_3, H_2SO_4 and CH_3COOH as acid media respectively. The influence of the kind of acid on the morphologies of the obtained $ZrWMoO_8$ was also investigated. All the chemical reagents were analytical grade purity without further purification. In the typical procedure, zirconium oxynitrate [$ZrO(NO_3)_2 \cdot 5H_2O$], ammonium tungstate [$N_5H_{37}W_6O_{24} \cdot H_2O$] and ammonium molybdate [$N_5H_{37}Mo_6O_{24} \cdot H_2O$] were dissolved separately in distilled water according to the mole ratio of Zr:W:Mo=1:1:1. First, W solution and Mo solution were mixed, and then Zr solution was added slowly under vigorous stirring. After that, acid solution (HCl, $HClO_4$, HNO_3, H_2SO_4, CH_3COOH(HOAc)) was added slowly to the above solution with continuous stirring for another 3 h. The

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mixture was finally loaded into a Teflon-lined Parr bomb and heated at 180 °C for 15 h. After natural cooling, the product was filtered, washed with distilled water, and dried at 60 °C. Cubic $ZrWMoO_8$ powders were obtained by calcining the precursor at a proper temperature varying from 500 °C to 600 °C for 6 h.

Products were characterized by powder X-ray diffraction using Cu Kα radiation (λ=0.15418 nm) (D/max2500, Rigaku). The XRD data were collected with a scan speed of $5°(2\theta)\cdot min^{-1}$ in the 2θ range from 10° to 50° by continuum scanning method. The samples' morphology and particle size were examined with PHILIPS XL-30ESEM scanning electron microscopy.

Figure 1a shows the XRD pattern of the precursor samples after hydrothermal treatment. In the present case, well crystallized precursor $ZrWMoO_7(OH)_2(H_2O)_2$ (JCPDS No.27-0994), an intermediate of the final product $ZrWMoO_8$, could be obtained in the HCl, $HClO_4$, HNO_3, H_2SO_4 and HOAc media. No obvious impurity can be detected. All the products after calcining have the same crystal structure no matter what the kind of acid used in synthesis of the precursor. The XRD pattern is shown in Fig. 1b, in which all diffraction peaks could be indexed to cubic β-ZrW_2O_8 (JCPDS No.50-1868). The high intensity of the diffraction peaks suggests that the products are well crystallized.

The morphologies of the $ZrWMoO_8$ samples obtained in the different acid medium were observed by SEM and the images are shown in Fig. 2. It can be seen that the morphology of $ZrWMoO_8$ particles was quite sensitive to the kind of acid medium. As shown in Fig. 2a, rod-like aggregates, which were made up by several nanorods connected to each other were obtained in the medium of HCl. The length of the products is up to 2 μm while the diameter is about 100–200 nm. In Fig. 2b, it can be seen that similar rod-like aggregates were obtained in the medium of $HClO_4$. Relatively large rod-like particles were obtained in the medium of HNO_3 as shown in Fig. 2c. The length is up to 7 μm and the diameter is about 500 nm. Irregular short rod-like particles were obtained in the medium of HOAc shown in Fig. 2d. When the acid medium changed to H_2SO_4, hexagon prism $ZrWMoO_8$ particles with uniform size were obtained (Fig. 2e).

It is interesting to note that similar results were obtained in the synthesis of TiO_2 using hydrothermal route [17]. It was reported that inorganic acid played a key role on the morphology of the resulted products, and preferentially adsorption of the anion controlled the growth rate of different crystal faces. In the present case, a possible growth mechanism is that Cl^- and ClO_4^- preferentially absorbed on the surfaces of $ZrWMoO_8$ crystal parallel to the *c*-axis, which restrained the growth in all directions except the *c*-axis, resulting in nanorods. And the rod-like particles were the products of the aggregation of those nanorods directed by high specific forces. While SO_4^{2-} may be absorbed on the side-surfaces at random tilt angles, cuboidal morphology was resulted and the exact mechanism should be further investigated.

Above discussions suggest that the morphology of the final products could be manipulated by adopting certain reaction conditions. In order to certify the effect of different anion on the morphology of final products, H_2SO_4 and HCl solutions were simultaneously used in the hydrothermal method. The morphologies of products obtained in mixed acids with different volume ratio were investigated. When volume ratio of HCl:H_2SO_4 changed from 0:1 to 1:1, the morphologies of the resulted products changed from hexagon prism to cuboid, as shown in Figs. 2e and 3a. The mean diameter and length of the cuboid are about 1 μm and 2 μm. When volume ratio of HCl: H_2SO_4 changed from 1:1 to 3:1, similar cuboid $ZrWMoO_8$ with an aspect ratio of 4 was obtained, while the average length of the cuboid is from 3 to 5 μm as shown in Fig 3b. It is worth noting that the mean diameter of the cuboid was approximately the same, while the corresponding length increased with the increasing amount

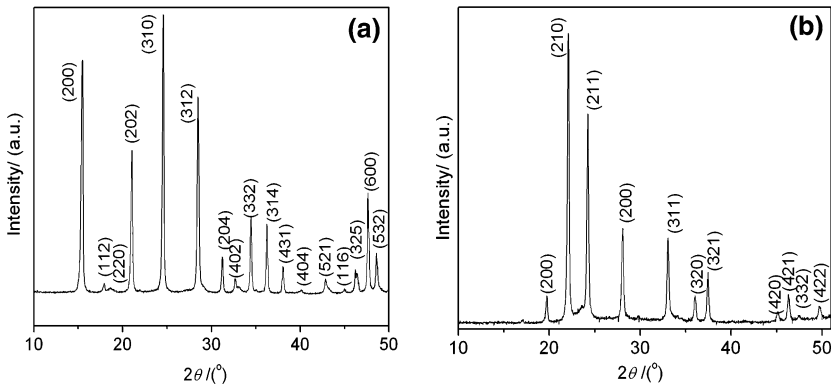

Fig. 1 XRD patterns of (**a**) precursor $ZrWMoO_7(OH)_2 \cdot 2H_2O$ and (**b**) cubic $ZrWMoO_8$

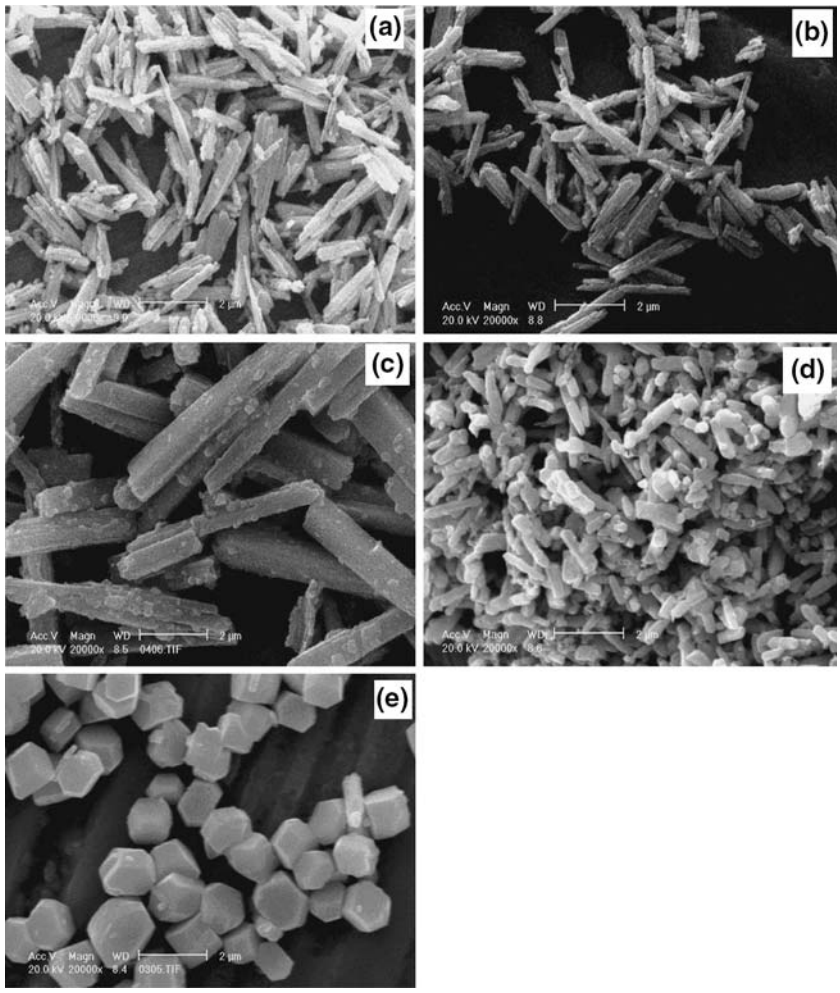

Fig. 2 SEM images of cubic $ZrWMoO_8$ prepared in different acid media: (**a**) HCl; (**b**) $HClO_4$; (**c**) HNO_3; (**d**) HOAc; (**e**) H_2SO_4

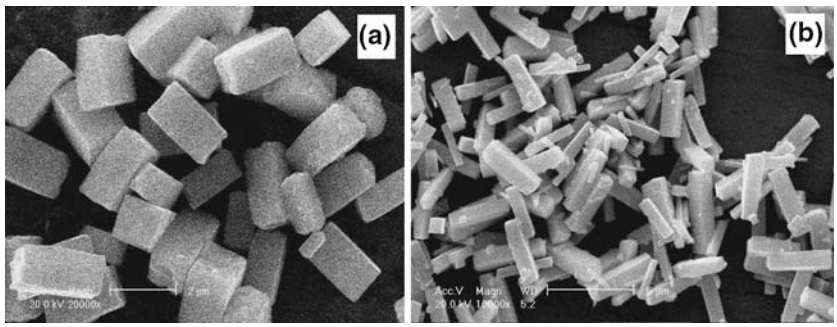

Fig. 3 SEM images of cubic $ZrWMoO_8$ prepared in different volume ratio of $HCl:H_2SO_4$ (**a**) 1:1; (**b**) 3:1

of HCl. These results indicate that it is possible to design the shape and size of $ZrWMoO_8$ according to their practical applications. However, the exact reason still needed to be further investigated and elucidated.

To the best of our knowledge, this is the first report of such hexagon prism and cuboid $ZrWMoO_8$ obtained by controlling the acid media. This approach towards controlling morphologies is promising, particularly because the wide range of accessible kinds of acids to be used.

In summary, pure phase cubic $ZrWMoO_8$ could be synthesized by hydrothermal method. Different morphologies of $ZrWMoO_8$ powders have been successfully achieved by changing the acid medium, and a serious of rod-like, hexagon prism and cuboid were obtained. These particles are promising candidates for materials science due to the importance of the shape and texture in determining various properties of materials [18]. Based on the results presented in this paper, it is speculated that the selective absorption on

various crystallographitcs faces of polyhedral of ZrW_2MoO_8 are crucial for determining the morphology, further work will be devoted to gain a deeper understanding on the detailed mechanism during this hydrothermal process.

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