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Preparation and characterization of $(V_{1-x}Al_x)_2O_3$ ultrafine powders by chemical doping method

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ABSTRACT

$(V_{1-x}Al_x)_2O_3$ ultrafine powders have been synthesized successfully by pyrolysizing poly-crystalline Al-doped precursor, Al-doped $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$ in H_2 atmosphere at 1373 K for the first time. The relation between the ratio of Al/V in the $VOCl_2$ solution and that in polycrystalline Al-doped precursor was studied. The result shows that this chemical doping method is successful, and the Al (III) content in precursor is controllable. The lattice parameters of $(V_{1-x}Al_x)_2O_3$ determined by XRD at room temperature and high-temperature reveal that the Al (III) enter the V_2O_3 lattice. The SEM micrograph shows that the size of the powder particles is about 100–200 nm. The DSC and magnetic susceptibility results of the $(V_{1-x}Al_x)_2O_3$ demonstrate that the powders exhibit the intrinsic phase transition properties.

1. Introduction

The V_2O_3 ceramics and single-crystal materials with good electrical and magnetic properties have been a subject of many investigations for a long time, because of their potential applications such as temperature sensors, protective and time delay switching and current regulation [1–5]. V_2O_3 exhibits a transition (AFI–PM) from low-temperature anti-ferromagnetic insulator (AFI) phase to high-temperature paramagnetic metal (PM) phase around 170 K. This phase transition is associated with abrupt changes in resistivity and magnetic susceptibility. For V_2O_3 doped by a small amount of Al (III), the transition temperature (T_c) of AFI–PM transition increases with the Al (III) content increasing, and a new transition appears from a low-temperature PM phase to a high-temperature paramagnetic insulating (PI) phase. The transition temperature of the new phase transition decreases with the dopant concentration increasing in a range of 188–400 K [6]. Hence, from a practical point of view, Al-doped V_2O_3 has more important significance than pure V_2O_3.

The PM–PI transition provides the potential for to be used as a functional positive temperature coefficient (PTC) material. Thus, $(V_{1-x}Al_x)_2O_3$ represents a kind of widely used electronic material because of its lower resistivity compared with $BaTiO_3$ at room temperature. This enables the $(V_{1-x}Al_x)_2O_3$ devices having very high rated current-carrying capacities and miniaturization [7,8]. Simultaneously, V_2O_3 system is a kind of useful catalyst [9,10], so $(V_{1-x}Al_x)_2O_3$ ultrafine powders maybe offer a new application as high-effect catalyst.

In general, V_2O_3 powder was prepared by reducing V_2O_5 in H_2 atmosphere, but only micro-powder about 10 μm in size could be obtained. So far although some works have been done on preparation of pure V_2O_3 ultrafine powder [11–14], reports about the synthesis of Al-doped V_2O_3 powders have never been discovered in the literatures. At present, $(V_{1-x}Al_x)_2O_3$ single-crystal and micro-grain ceramics have been prepared, but the preparing condition of these two kinds of materials was very rigorous. $(V_{1-x}Al_x)_2O_3$ single-crystal was prepared by arc melting a mixture of V_2O_3 and Al_2O_3 at very high-temperature [6,15]. $(V_{1-x}Al_x)_2O_3$ ceramics was obtained as follows: a mixture of V_2O_3 and Al_2O_3 was ball-milled for a long time, pressed into disc, then sintered at 1773 K in H_2 atmospheres for 10 h. The grains in the ceramics obtained by above method were about 10 μm in size and the process demanded more energy and longer time. Moreover, the micro-crack would appear easily in $(V_{1-x}Al_x)_2O_3$ large-grain ceramics during thermo-cycles because of its large transition stress, that resulted in the electrical property instability [7,8,16,17]. These problems could be solved by decreasing grain sizes in ceramics. Preparing the $(V_{1-x}Al_x)_2O_3$ ultrafine powder may become the key step in the process of preparation of fine grain ceramic.

In our previous work [18], we reported the preparation of $(V_{1-x}Cr_x)_2O_3$ nano-powder by pyrolysizing of Cr-doped $(NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$, in H_2 flow. In this paper, we obtained $(V_{1-x}Al_x)_2O_3$ ultrafine powder at lower temperature (1373 K) successfully.

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2. Experiment details

The growth of single-crystalline Al-doped precursor was similar to that of the undoped sample detailed in our previous work: [19]

$$VOCl_2 + AlCl_3 + NH_4HCO_3 \rightarrow \text{Al-doped } (NH_4)_5[(VO)_6(CO_3)_4(OH)_9]\cdot 10H_2O$$

The size of the obtained single-crystal was about 2–3 mm with dark violet color. The synthesis of polycrystalline Al-doped precursor was also similar to that described in the literature [12]. $(V_{1-x}Al_x)_2O_3$ powder was obtained by heating polycrystalline Al-doped precursor in H_2 flow at 1373 K for 1.5 or 5 h.

$(V_{1-x}Al_x)_2O_3$ powder samples were dissolved in a mixed solution of vitriol and phosphoric acid. The Al contents in solutions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). X-ray diffraction (XRD) pattern was recorded on a D/max-2200 diffraction using Cu $K\alpha_1$ radiation (λ = 0.154050 nm) and corundum Al_2O_3 was used as an inner standard. The experiments were done in Ar atmosphere to avoid reoxidation of the $(V_{1-x}Al_x)_2O_3$. The morphology of the powders was observed on a JSM-6330 field emission scanning electron microscope (SEM). Differential scanning calorimetry (DSC) experiments were performed on a Netzsch DSC-204 in N_2 atmosphere in a range of 100–400 K with a heating rate of 10 K/min. Magnetic susceptibility measurements was carried out using a SQUID magnetometer in a range of 80–400 K with 50 kOe magnetic density.

3. Results and discussion

Al-doped single-crystal precursors were washed by saturated NH_4HCO_3, distilled water for three times to remove adsorptive impurity, and then dissolved in a dilute hydrochloric acid solution, and their content of Al (III) was determined. The results showed that the ratio of Al/V in the precursors was 0.0330 and 0.0410 when Al/V in $VOCl_2$ solution was 0.0200 and 0.0300, respectively. In addition, it was affirmed that Al-doped precursor was single-crystal by four-circle diffractometer. But the analysis of single-crystal could not determine the site of Al (III) in precursor lattice because the Al content was very low. According to this method, we could obtain polycrystalline Al-doped precursors. The method would create a favorable conditions to prepare $(V_{1-x}Al_x)_2O_3$ powders.

Fig. 1 shows the effect of the Al/V in $VOCl_2$ solution on that in polycrystalline precursors when the growth time of precursors is 2 h. From Fig. 1, the dopant concentration in polycrystalline precursors was in proportion to that in $VOCl_2$ solution. Fig. 2 exhibits the dependence of the Al/V ratio in the precursors on the growth time of precursor crystal in solution when Al/V ratio in $VOCl_2$ solution is 0.0100. The result also showed that the ratio of Al/V in the precursors was proportional to the growth time of precursor crystal. So the Al/V ratio in polycrystalline precursor could be controlled accurately by adjusting the Al/V in $VOCl_2$ solution and the growth time of precursor crystal.

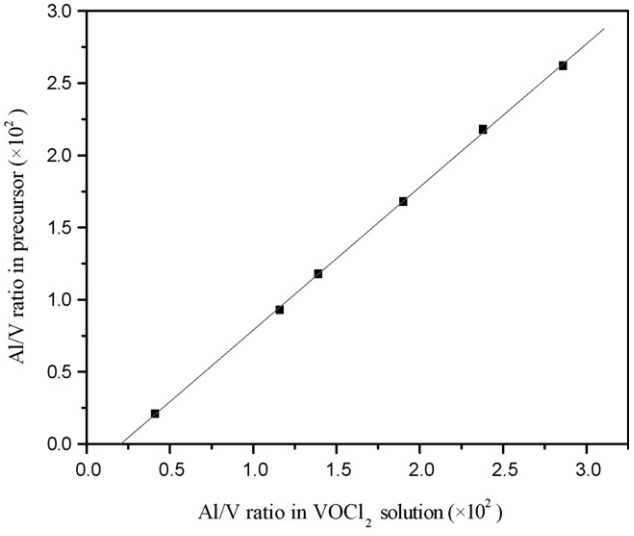

Fig. 1. The relationship between the Al/V ratio in precursors and that in $VOCl_2$ solution when the growth time of precursors is 2 h.

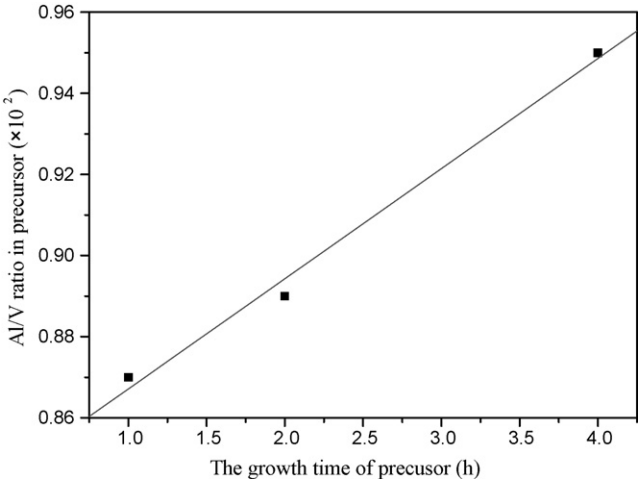

Fig. 2. The effect of growth time of crystal in solution on the Al/V ratio in precursors when Al/V ratio of 0.0100 in $VOCl_2$ solution.

The room temperature XRD patterns of $(V_{1-x}Al_x)_2O_3$ powders are shown in Fig. 3. The unit-cell parameters obtained from Fig. 3 using the program ERACEL written by Laugier are presented in Table 1. The parameter a increased and c decreased with the Al concentration increasing in $(V_{1-x}Al_x)_2O_3$, which is similar to $(V_{1-x}Cr_x)_2O_3$ single-crystal [20]. It can be seen from (1 1 0), (1 1 3), (2 1 4) and (3 0 0) peaks that $(V_{1-x}Al_x)_2O_3$ ($x < 0.016$) contained both PM and PI phases (see Fig. 3b and c), pure V_2O_3 contained only PM phase (see Fig. 3a). Moreover, the intensity of PI phase increased and the intensity of PM phase decreased with the Al content increasing in $(V_{1-x}Al_x)_2O_3$. But when x = 0.019 (see Fig. 3d) only PI phase existed and PM phase disappeared because of the T_c decrease with Al content increasing. These results are same as those of $(V_{1-x}Al_x)_2O_3$ single-crystalline [6].

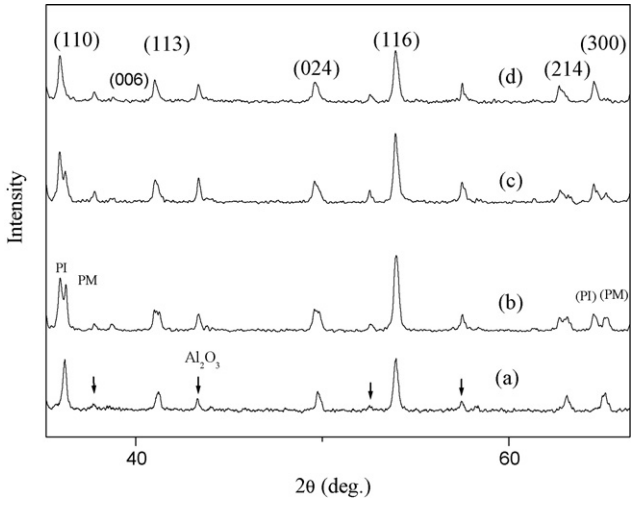

Fig. 3. Room temperature XRD patterns of (a) V_2O_3, (b) $(V_{0.992}Al_{0.008})_2O_3$, (c) $(V_{0.991}Al_{0.009})_2O_3$ and (d) $(V_{0.981}Al_{0.019})_2O_3$ powders obtained from pyrolysizing precursors at 1373 K for 1.5 h. The arrows denote the peaks of corundum Al_2O_3.