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Hollow tubular potassium magnesium titanate with high thermal stability

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ABSTRACT

Hollow tubular potassium magnesium titanate (KMTO) were synthesized using $Mg(OH)_2$, $TiO(OH)_2$ and K_2CO_3 as the raw materials and KCl as the flux. We studied the thermal stability of the KMTO and the reflectivity in the near-infrared wavelength range of KMTO treated at different temperatures. The results indicated that hollow tubular KMTO powders 4–15 μm in length and 1–2 μm in diameter could be obtained after being calclined at 850 °C for 2 h. The resulting KMTO powders had good thermal stability in structure and near-infrared reflectivity. Only a small amount of KMTO decomposed into $MgTi_2O_5$ and TiO_2 when the as-calcined powders were post heat-treated at 1500 °C. Moreover, the high temperature treatment had only a minor effect on the high near-infrared reflectivities of KMTO. The results indicated that the prepared KMTO exhibited excellent thermal stability.

1. Introduction

Potassium hexatitanate whiskers have low thermal conductivity and high near-infrared reflectivity, which favors their use in the manufacture of heat-insulating materials and coatings [1–3]. Many synthetic strategies have been described to obtain $K_2Ti_6O_{13}$ whiskers including high-temperature calcination [4,5], sol-gel method [6], flux method [7], hydrothermal method [8], etc. In addition, the structural and thermal stability are the key metric to evaluate heat-insulating materials at the high temperatures. Previously, Qi et al. studied the thermal stability of potassium titanate whiskers and showed that $K_2Ti_6O_{13}$ transformed to $K_2Ti_4O_9$ at 1100 °C. The thermal stability of $K_2Ti_6O_{13}$ decreased after calcining at 1200 °C [4].

In recent years, the structure of potassium magnesium titanate (KMTO) with hollandite has been shown to be similar to potassium hexatitanate [9,10]. Because of its special crystal structure, KMTO with hollandite has utility in friction, insulation, superionic conductor materials [11–15], etc. Our recent work demonstrated that KMTO whiskers have high near-infrared reflectivity and low thermal conductivity. This offers many applications as heat-insulating materials [13]. In addition, it is very essential to study these materials' stability in structure and the near-infrared reflection property.

This work evaluates the structure and near-infrared reflection properties of heat-treated KMTO. It offers insights into the thermal stability of the calcined KMTO and suggests their role as heat-insulation materials.

2. Experimental

KMTO were synthesized via the flux method using the same process as described in our previous work [13]. However, the $TiO(OH)_2$ was used as a titanium source rather than TiO_2. The starting materials included analytically pure K_2CO_3, $Mg(OH)_2$ and $TiO(OH)_2$ (at a molar ratio of Ti:Mg:K = 7:1:2). These were mixed with KCl, and the molar ratio of KCl/reactants is 1:1. The mixtures were dried at 80 °C for 8 h and then calcined at 850 °C for 2 h. After cooling to room temperature, the products were washed with distilled water to remove KCl (detected with $AgNO_3$ solution) and then dried at 100 °C for 10 h. Subsequently, some of the as-calcined powders were post heat-treated at 1000–1500 °C for 2 h.

The crystalline phase, morphology and chemical composition of the powders were examined by X-ray diffraction (XRD, X'Pert Pro MPD, Philips, Netherland) and scanning electron microscopy (FESEM, Nova400 NanoSEM, FEI company, USA) equipped with energy-dispersive X-ray spectroscopy (EDS) analysis system, respectively. The high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were evaluated on JEM-2100UHR TEM (JEOL, Japan). The thermal stability of the as-calcined powders was measured by a thermal analyzer (STA

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449C, Netzsch, Germany) from 20 to 1550 °C at 10 °C/min in air. The reflectivities of the as-calcined and heat-treated powders were then analysized from 200 to 2600 nm with UV–VIS-NIR spectrophotometer (U-4100, HITACHI, Japan).

3. Results and discussion

Fig. 1 (a) shows the XRD patterns of the powders recovered from the flux at 850 °C for 2 h. The main phase is KMTO (JCPDS No. 84-0974) of hollandite structure with a trace amount of $MgTiO_3$. Fig. 1(b) and (c) show the corresponding FESEM images and EDS profile of the calcined powders, respectively. Fig. 1(d) shows the corresponding TEM image. Hollow tubular prismatic powders with lengths of 4–15 μm and diameters of 1–2 μm were obtained. EDS analysis presents K, Mg, Ti, O elements are approximately stoichiometry of $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$. The SAED patterns as shown in the inset of Fig. 1(d) indicates calculated fringe spacing values of 2.86 Å, 2.23 Å and 5.09 Å that correspond to the (1 0 1), (3 0 1) and (2 0 0) interplanar distance of $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$ (JCPDS No. 84-0974), respectively. A two-dimensional HRTEM image is presented in Fig. 1(e). The fringe spacing was 5.10 Å in coincidence with the (2 0 0) interplanar distance of $K_{1.54}Mg_{0.77}Ti_{7.23}O_{16}$.

Fig. 2(a) shows the XRD patterns of KMTO heat-treated at different temperature. When the as-calcined KMTO were heat-treated at 1000–1500 °C, the main phase is KMTO (JCPDS No. 84-0974) of hollandite structure. The weak diffraction peaks of $MgTi_2O_5$ and TiO_2 indicated that only a small amount of the KMTO had decomposed when the post treatment temperature reaches 1500 °C.

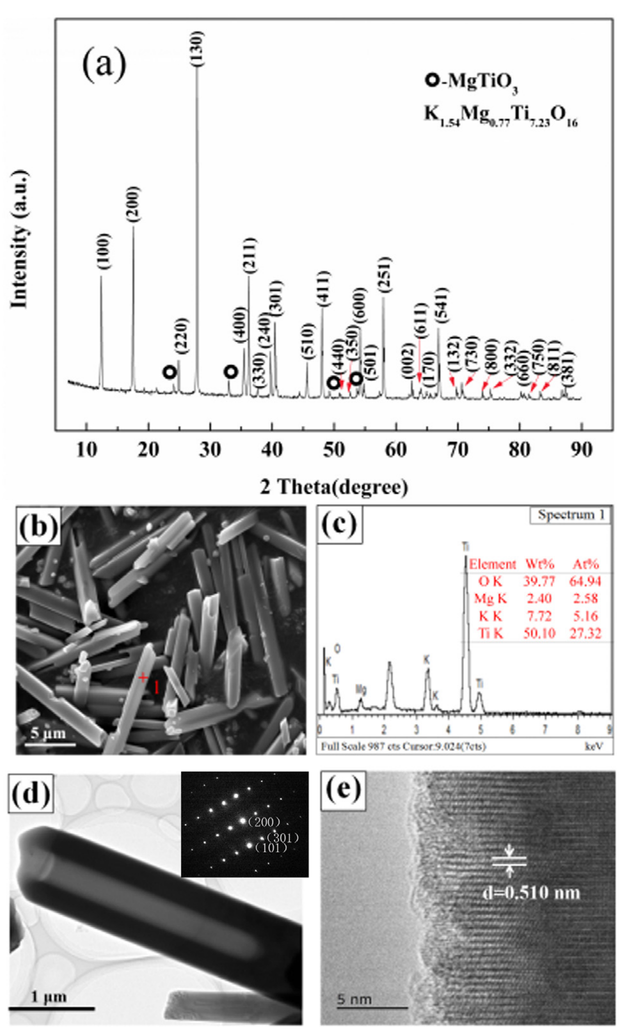

Fig. 1. (a) XRD patterns of the powders as-calcined at 850 °C for 2 h. (b) The corresponding FESEM images, (c) EDS profile of point 1 marked with "+" in (b), (d) TEM image and selected area electron diffraction (SAED), (e) HRTEM image.

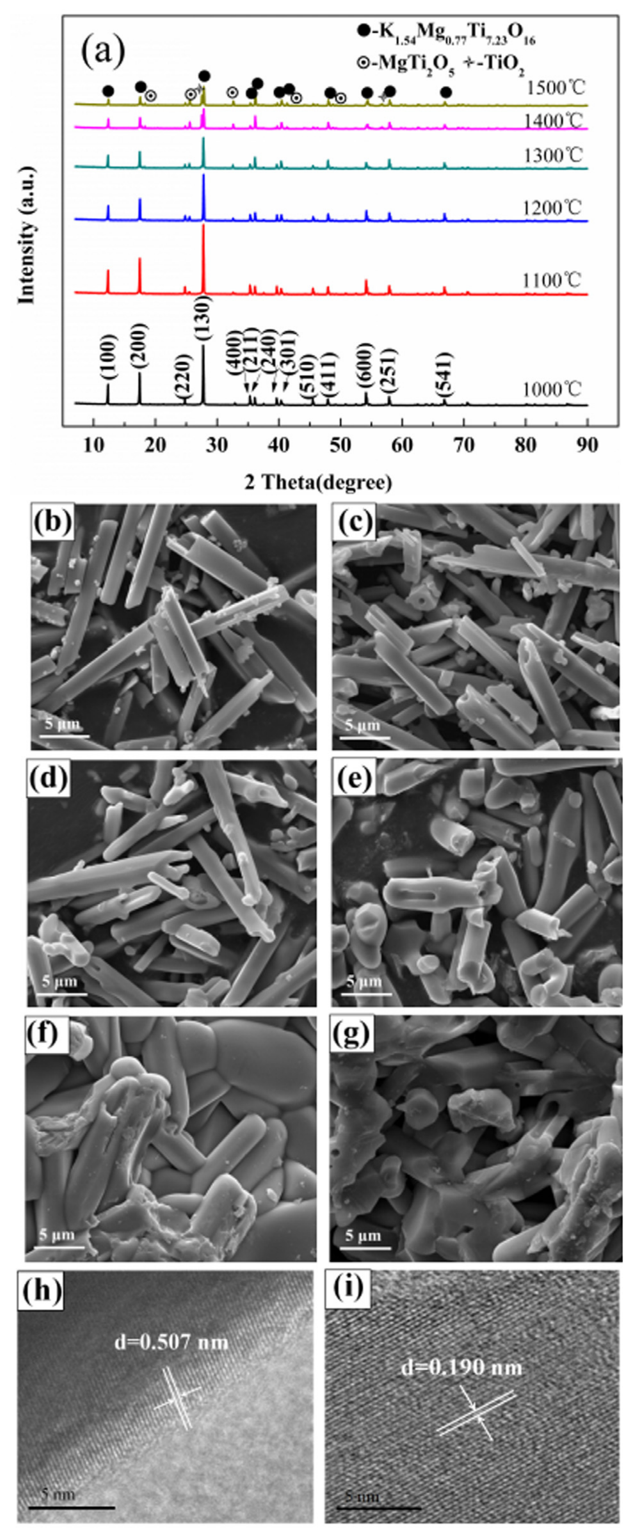

Fig. 2. (a) XRD patterns of KMTO heat-treated at different temperature. The corresponding FESEM images: (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C, (f) 1400 °C, (g) 1500 °C. The corresponding HRTEM images: (h) 1300 °C, (i) 1500 °C.