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Synthesis of Titanate Nanotubes from Thai Leucoxene Mineral

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Abstract

Titanate nanotubes were synthesized by hydrothermal method at 105 °C for 24 h (setting temperature) using natural leucoxene mineral as the starting material. The samples were characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM). The prepared nanotubes showed internal diameter of 4-6 nm, external diameter of 8-10 nm, and the length of 0.2-1 μm. This synthesis method provided a simple route to fabricate nanostructured material from low cost natural mineral using Thai autoclave unit.

Keyword: Nanotube; Hydrothermal; Leucoxene; TiO_2

1. Introduction

Over the past decades, one-dimentional nanostructured materials derived from titanium dioxide (TiO_2) and titanate has been attended for various applications such as semiconductor materials, dye sensitized solar cells, water treatment materials, catalyst material, gas sensor, and so on [1-5]. Titanate nanotubes have been product by several methods such as sol-gel, electro-spinning, template controlled solid-state, chemical vapor deposition (CVD), and etc. Each method has both advantages and disadvantages depending on the implementation [6-10].

After the pioneer work on TiO_2-related nanotubes preparation by Kasuga et al. [6, 11] the hydrothermal method in alkali solution has become one of the most powerful techniques to prepare a wide range of TiO_2-related one-dimensional (1-D) nanostructured.

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Due to the high cost of commercial TiO_2 nanoparticles, synthesis of titanate nanotubes from natural leucoxene mineral by hydrothermal method was investigated. The aim of this study is to prepare nanotubes via simple hydrothermal method from low-cost Thai leucoxene mineral using autoclave unit that was design and built at Rajamangala University of Technology Thanyaburi (RMUTT). The crystal structures and the microstructure of titanate nanotubes will be reported in detail.

2. Experimental Procedure

2.1. Preparation of TiO_2 powders

Titanate nanotubes were prepared from a low cost Thai natural leucoxene mineral as the starting material. In a typical preparation, 10 g of the natural leucoxene mineral (reduced size) was put into a Teflon-lined stainless steel autoclave with internal capacity of 4000 ml (Thai made) (Fig. 1). Then, the autoclave was added with 2000 mL of 10M NaOH aqueous solution followed by hydrothermal treatment of the mixture at 105 °C for 24 h (setting temperature) with stirring condition. After hydrothermal reaction, it was cooled to room temperature, the precipitate was separated by filtration and washed with 500 ml of 0.1M HCl solution and 500 ml distilled water for several times until the pH value of the rinsing solution reached ca. 7. The washed samples were dried in the oven at 100 °C for 12 h.

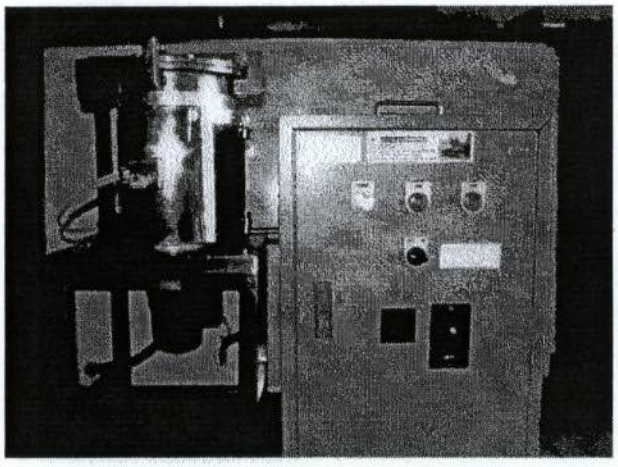

Fig. 1. Autoclave and control unit (Thai made)

2.2. Characterization

The shape and size of the starting natural leucoxene mineral and as-synthesized sample were obtained by transmission electron microscopy (TEM, JEOL JEM-2010). The crystalline structures of the starting natural leucoxene mineral and as-synthesized sample were analyzed by X-ray diffraction (XRD, PANalytical X'Pert PRO MRD).

3. Results and Discussion

SEM images of the starting natural leucoxene mineral in Fig. 2 show the granules size about 75-300 μm (Fig. 2a) and about 20-50 μm (Fig. 2b) after reduced the size by ball mill. The chemical composition of natural leucoxene minerals was analyzed by X-ray fluorescence techniques (XRF). The main component of natural leucoxene minerals is a titanium dioxide (TiO_2) about 93.013%.

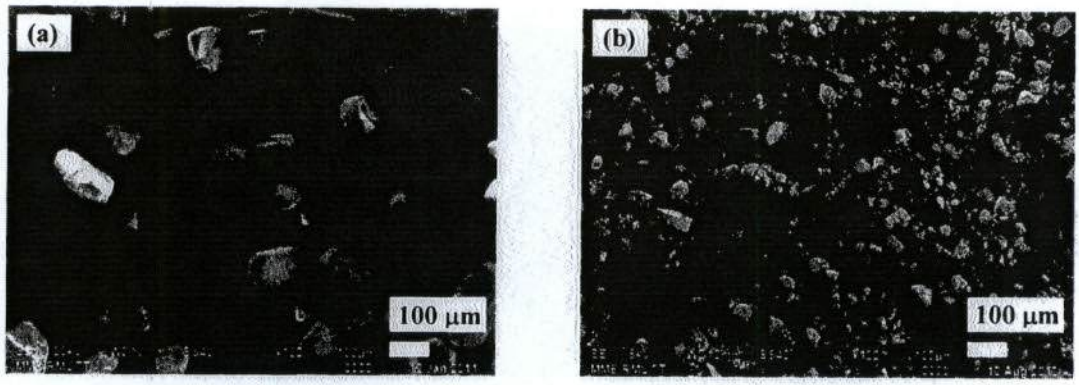

Fig. 2. SEM images of the starting natural leucoxene mineral, (a) before ball milling and, (b) after ball milling

The X-ray diffraction result shown in Fig. 3 indicates that the starting natural leucoxene mineral consists of the mixed rutile and anatase phase. The peaks of the prepared sample observed at 2θ~10°, 24°correlated to the hydrogen titanate ($H_2Ti_3O_7$) [11-13].

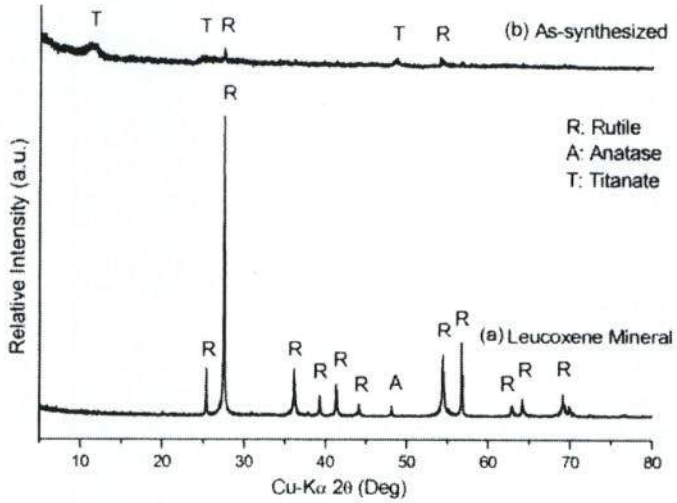

Fig 3. XRD patterns of (a) the starting natural leucoxene mineral, (b) the as-synthesized sample

There is a general agreement that the reaction proceeds through several stages: (1) slow dissolution of raw TiO_2 accompanied by epitaxial growth of layered nanosheets of sodium titanates, (2) exfoliation of the nanosheets, (3) folding of the nanosheets into tubular structures (seeds), (4) growth of the nanotubes along the axis, (5) exchange of sodium ions by protons during washing and separation of nanotubes [14]. In fact, the nanotubes are composed of layers of the titanate, which depends on the synthesis conditions such as applied temperature, and treatment duration, and the residue of sodium. The resulting product may occur in the form of $H_2Ti_3O_7$ and $Na_xH_{2-x}Ti_3O_7$ [6, 10, 14]. The crystalline of raw material is first converted to an amorphous product through alkali treatment, and subsequently, titanate nanotubes are formed after treatment with distilled water and HCl aqueous solution [6, 15].

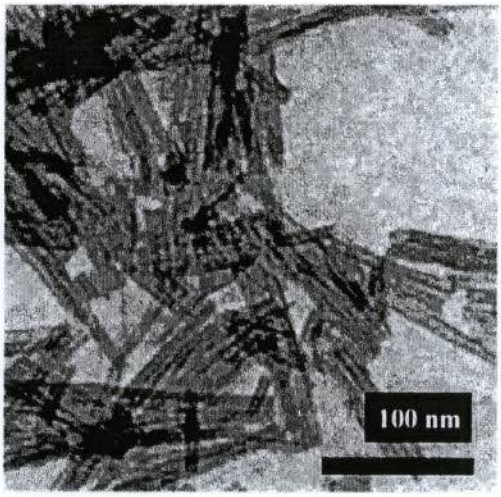

Fig. 4. TEM images of the as-synthesized sample

Fig. 4 show the TEM image of the as-synthesized nanotubes sample. Fig. 4 shows the hollow tubular nanostructures of the prepared titanate nanotubes. The prepared titanate nanotubes showed the average outer diameter of around 8–10 nm, and inner diameter around 4–6 nm, and the length of around 0.2-1 μm.

4. Conclusion

In summary, titanate nanotubes were synthesized by hydrothermal method using low-cost natural leucoxene mineral as the starting materials at 105 °C for 24 h. (setting temperature). The prepared titanate nanotubes showed internal diameter of 4-6 nm, external diameter of 8-10 nm, and the length of 0.2-1 μm. This preparation method provided a simple route to fabricate titanate nanotubes from low-cost material using Thai autoclave unit.

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