Journal of Electrostatics 72 (2014) 353–356

Contents lists available at ScienceDirect

Journal of Electrostatics

journal homepage: www.elsevier.com/locate/elstat

Preparation and vibrational spectra of wollastonite-type $CaGeO_3$ microtubes by electrospinning

Zhenwei Yu, Zhaochun Zhang*, Huiyi Jiang, Jun Zhao, Shanshan Yang

School of Material Science and Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 10 September 2013
Received in revised form
23 March 2014
Accepted 27 June 2014
Available online 9 July 2014

Keywords:
Electrospinning
Microtubes
Vibrational spectra
Nuclear site group analysis

ABSTRACT

In the present paper, we synthesized the novel calcium germanate ($CaGeO_3$) microtubes using electrospinning. The wollastonite structure and morphology of the novel $CaGeO_3$ microtubes have been confirmed by X-ray diffraction and scanning electron microscopy, respectively. The Raman and infrared spectra of this oxide were recorded and analyzed at room temperature. Then, nuclear site group analysis was used to calculate the total number of normal vibrational modes, Raman-active and infrared-active optical phonon modes.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, much attention has been paid on nano or microscale materials including nanocomposite films, nanosheets, nanowires, nanoparticles and microtubes because they show unique properties [1–5]. Wollastonite-type $CaGeO_3$ has been synthesized successfully by mixture of reagent-grade powders of $CaCO_3$ and GeO_2 by heating at 1473 K for many hours [6–11]. Nevertheless, this method need high temperature, long reaction time due to the high demand of activation energy and the $CaGeO_3$ prepared by this method usually didn't have novel morphologies. Hence, it is very meaningful to find new routes for synthesis of novel wollastonite-type $CaGeO_3$. One of the new routes may be electrospinning, by which various kinds of one-dimensional materials have been synthesized successfully, such as polymer nanofibers [12], $CaGa_2O_4$ nanofibers [13], SnO_2/ZnO composite nanofibers [14].

Electrospinning is a method of producing superfine fibers with diameters ranging from 10 μm down to 10 nm [15]. To date, electrospinning is broadly applied in industries because of its advantages such as cost effectiveness, good repeatability, large-scale production and ability to make various morphologies [16]. In this paper, we report a technique to prepare $CaGeO_3$ microtubes using electrospinning. The structure and morphology of as-prepared $CaGeO_3$ were confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), Raman spectroscopy and infrared spectroscopy, respectively. Moreover, nuclear site group analysis [17] was used to calculate the total lattice vibration modes in order to verify the validity of the structural data drawn from XRD analysis.

2. Experimental

2.1. Materials

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) (99.0%), ethanol (99.7%), acetylacetone (98.5%) and polyvinyl pyrrolidone (PVP, $M_w = 1{,}300{,}000$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Germanium(IV) iodide (GeI_4) was prepared from germanium dioxide (GeO_2) by reaction with concentrated hydriodic acid [18].

2.2. Preparation of wollastonite-type $CaGeO_3$ by electrospinning

Firstly, the solution was prepared by dissolving 1.4700 g (6.2288×10^{-3} mol) of $Ca(NO_3)_2 \cdot 4H_2O$ and 3.6508 g (6.2288×10^{-3} mol) of GeI_4 in the mixture of 20 mL of ethanol and 20 mL of acetylacetone. Subsequently, 2.0 g of PVP was slowly added into the solution under continuous stirring for 4 h to obtain a homogeneous viscous spinning solution.

In a typical electrospinning process, the as-prepared precursor solution was immediately loaded into a couple of 20 mL capacity

---

* Corresponding author.
E-mail address: zhangzhaochun@shu.edu.cn (Z. Zhang).

http://dx.doi.org/10.1016/j.elstat.2014.06.007
0304-3886/© 2014 Elsevier B.V. All rights reserved.

plastic syringe equipped with a 23-gauge stainless steel needle. The flow rate through the needle, controlled by a syringe pump, was 0.8 mL/h. The schematic setup of our electrospinning setup is shown in Fig. 1. The distance between the spinneret and collector was fixed at 9 cm. The positive terminal of a variable high-voltage power supply was connected to the needle tip of the syringe, and the negative terminal was connected to a piece of aluminum foil used as the collector. Upon the application of a high voltage of about 11 kV across the needle and the collector plate, a fluid jet was ejected from the nozzle and the Taylor cone was observed. When the high voltage was slightly increased, the jet accelerated towards the collector, the solvent evaporated, leaving only ultrathin fibers on the collector. Finally, the electrospun fibers were placed in a silica desiccator at room temperature and calcined in air at 850 K for 4 h with a heating rate of 3 °C/min.

The prepared material was characterized by XRD (D/MAX-RC model diffractometer) with the use of CuKα radiation ($\lambda = 0.15418$ nm). The morphology analysis was carried out with SEM (JSM-6700F, JEOL). The chemical bonding in the material was studied by Raman spectroscopy (excitation wavelength of 514.5 nm, Renishow Invia plus) and Fourier Transform Infrared Spectroscopy (FTIR) using an Avatar 370 spectrometer (Nicolet Instrument Corporation) working in the mid-infrared range from 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Structural and morphological characteristics

Typical XRD pattern of obtained sample are shown in Fig. 2. From Fig. 2, the strongest diffuse reflection centered at 29.14°, which can be assigned to the (021) reflection of a wollastonite-type $CaGeO_3$ (JCPDS No. 086–1875). $CaGeO_3$ is isostructural with $CaSiO_3$, wollastonite-IT, and crystallizes in the $P\bar{1}$ space group with the cell parameters: $a = 7.269(2)$ Å, $b = 7.526(2)$ Å, $c = 8.094(2)$ Å, $\alpha = 103.44(3)°$, $\beta = 94.42(3)°$, $\gamma = 90.11(3)°$, $Z = 6$ [7]. Fig. 3(a) shows the unit cell and atomic nomenclature of wollastonite-type $CaGeO_3$. The unit cell contains two chains of tilted GeO_4 tetrahedral groups along b-axis with calcium atoms inserted between them. The essential feature of the structure is the linkage of the GeO_4 tetrahedra by sharing two of the four corners to form continuous chains of composition $(GeO_3)_n$ (Fig. 3(b)).

The SEM images in Fig. 3(c) and (d) show the morphologies of the wollastonite-type $CaGeO_3$. It can be observed from Fig. 3(c) that a large amount of one-dimensional wires with diameters of about 2–4 μm and lengths of several hundred μm can be easily observed for $CaGeO_3$. Further observation from Fig. 3(d) indicates that the microwires have a hollow, tube-like structure. The novel $CaGeO_3$ microtubes may have potential applications in the future.

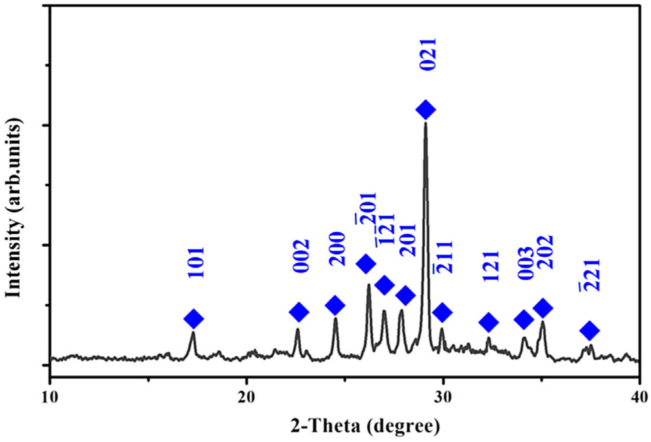

Fig. 2. XRD pattern of $CaGeO_3$.

3.2. Nuclear site group analysis

Nuclear site group analysis was developed by Mathieu to treat molecules. The method is extended to crystals and is presented in conjunction with a set of tables to greatly ease the burden of selection rule determination [17]. For a complete introduction see Roussrau [17].

The $CaGeO_3$ triclinic belongs to the $P\bar{1}$ symmetry group (No. 2); $Z = 6$ [7]. Ca, Ge and O are distributed in 2(i) positions. Table 1 shows the Atomic Wyckoff positions and reducible representations for $CaGeO_3$ oxide at the Γ point. The Ca, Ge and O atoms occupy C_1 sites will contribute $3A_g + 3A_u$ symmetry mode, respectively. The total symmetry mode: $\Gamma = 45A_g + 45A_u$. After subtraction of the A_u acoustical mode, the optical modes lead to the following representation: $\Gamma_{opt} = 45A_g(R) + 44A_u(IR)$. It is clear that there are no more than forty five and forty four theoretically observable Raman peaks and FTIR absorption bands, respectively.

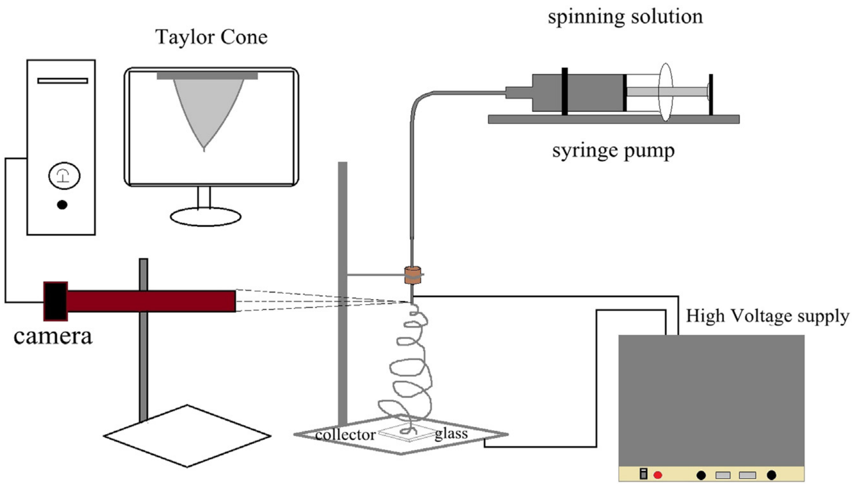

Fig. 1. Schematic diagram of our electrospinning setup.

Download English Version:

https://daneshyari.com/en/article/726495

Download Persian Version:

https://daneshyari.com/article/726495

Daneshyari.com