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静电纺丝结合溶胶–凝胶法制备 $MgNb_2O_6$ 陶瓷纤维

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摘要: 以五氧化二铌(Nb_2O_5)和氧化镁(MgO)为原料,柠檬酸作配位剂,采用静电纺丝结合溶胶–凝胶法制备了铌酸镁($MgNb_2O_6$)陶瓷纤维。在本合成体系中, 高质量 Nb^{5+}溶液的获得是形成 $MgNb_2O_6$ 前驱体溶胶的关键步骤。通过 TGA,FTIR,XRD,TEM 以及 SEM 技术对纤维的形貌,微观结构以及组成进行了表征。结果表明,900 ℃烧结以后得到的 $MgNb_2O_6$ 纤维长度约为 10 cm,具有中空结构,壁厚约为 800 nm。

关键词: $MgNb_2O_6$; 纤维; 静电纺丝; 合成
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Synthesis of $MgNb_2O_6$ Ceramic Fibers by Electrospinning with Sol-gel Process

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Abstract: $MgNb_2O_6$ ceramic fibers were synthesized using niobium oxide and magnesium oxide as starting materials by the electrospinning with sol-gel process. Citric acid was used as the chelating reagent to coordinate to the metal ions. The key step to the formation of $MgNb_2O_6$ precursor sols is to obtain a high quality solution of Nb^{5+}. The morphology, structure, and composition of $MgNb_2O_6$ fibers were characterized by TGA, FTIR, XRD, TEM and SEM techniques. The results show that $MgNb_2O_6$ fibers calcined at 900 ℃ with length in the order of 10 cm have the hollow structure and are composed of nanoparticles (particle size <100 nm) and the thickness of the wall is no more than 800 nm.

Key words: $MgNb_2O_6$; fiber; electrospinning; synthesis

0 Introduction

With the recent progress of microwave communication systems, miniaturization of microwave components for volume efficiency is a major research requirement. To develop these microwave materials, the controlled morphologies and lower sintering temperatures will play an important role in the future. Magnesium niobate ($MgNb_2O_6$) belongs to a binary niobate compounds with general formula of MNb_2O_6 (M=Mg, Zn, Co, Ni and Cu etc.) and exhibits excellent dielectric properties and is identified as a potential candidate to be used as microwave dielectric materials due to their low dielectric loss and high dielectric constant [1]. Furthermore, $MgNb_2O_6$ is also known as a key precursor material for the preparation of single-phase relaxor ferroelectric perovskite ($Pb(Mg_{2/3}Nb_{1/3})O_3$) which is becoming increasingly important for transducer, electrostrictor and actuator applications [1-2]. However, $MgNb_2O_6$ is generally prepared by the

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traditional solid-state route which needs very high sintering temperature resulting in inhomogeneous composition, irregular grain shape, and larger grain size with broad distribution[3-6]. Furthermore, $Mg_4Nb_2O_9$ and/or MgO phases are sometimes formed alongside the major phase of $MgNb_2O_6$[7-8].

Up to now, several groups have focused their work on the synthesis of $MgNb_2O_6$ ceramic materials by wet-chemical methods, such as co-precipitation[9-10], sol-gel process [11-12] and polymerized complex method [13]. Although great interests in zero-dementional nanomaterials have been focused on controlling the morphology of materials and the related novel properties, it is difficult in direct application of these materials due to the inconvenience in manipulation. On the contrary, the one-dimensional (1D) nanofibers offer advantages in direct technological applications, which can work as micro-reactor or micro-filtration used in biology, and can be implanted with other materials giving a host-guest material [14]. Nowadays, the electrospinning technique has received considerable attention because of its simplicity and versatility for fabrication of 1D nanostructures in recent years[15-17].

The fiberization of $MgNb_2O_6$ materials will expand their applications and enhance properties in many fields. Long fibers are attractive for their special properties in multifunctional composite materials because they could provide increased anisotropy and specific strength over monoliths as well as excellent flexibility [18]. To the best of our knowledge, there have been no reports on $MgNb_2O_6$ fibers prepared by the electrospinning method. In our present work, $MgNb_2O_6$ ceramic fibers are prepared by means of a simple electrospinning combined with sol-gel method. The key step for this method is to remove F^- from the solution by adding $NH_3{\cdot}H_2O$ when Nb_2O_5 is dissolved in HF acid, which can form the white $Nb(OH)_5$ precipitation and avoid the existence of F^- in processing of the formation of sol-gel. It is important to obtain a high quality solution of Nb^{5+} for the formation of $MgNb_2O_6$ precursor sols. This process involves the complexation of metal ions by citric acid having one hydroxyl group and avoids complex steps such as refluxing of alkoxides.

1 Experimental

For preparing $MgNb_2O_6$ ceramic fibers, high pure niobium (V) oxide powders, HF (40%), magnesium oxide and ammonia was used as starting materials. The citric acid monohydrate (CA) was used as a chelating agent and reaction medium.

1.1 Preparation of Nb-citric acid complex

2.66 g Niobium oxide pentahydrate (Nb_2O_5) was dissolved in 22.8 g HF after heating in hot water bath for 20 hr to form a transparent solution, and in order to remove the F^- from the solution, ammonia was added to adjust the pH value to 10, then the white $Nb(OH)_5$ precipitation can be obtained. The niobium hydroxide precipitated was filtered and washed to eliminate ammonium and F^- and dissolved into the citric acid (CA) aqueous solution (c_{CA}/c_{Nb}=2).

1.2 Preparation of Nb-Mg precursor sols

The Mg-Nb precursor sols were prepared using Nb-citric acid complex in an aqueous solution. Magnesium oxides was slowly added to Nb-citric acid complex, with the precise stoichiometric ratio ($c_{Mg(II)}/c_{Nb(V)}$ =0.5) in the acid solution. Solution was stirred for 3 h at 70 ℃ to obtain the Nb-Mg precursor sols. The sols were aged at 60 ℃ until the homogeneous viscous solution was obtained.

The schematics of the electrospinning apparatus is shown in Fig.1. The viscous solution was drawn into a stainless steel capillary with inner diameter of 0.45 mm and outer diameter of 0.50 mm. The positive terminal of a variable high-voltage power supply (BGG-200 kV/20 mA) was connected to the needle tip of the capillary while the other was connected to the collector plate. In

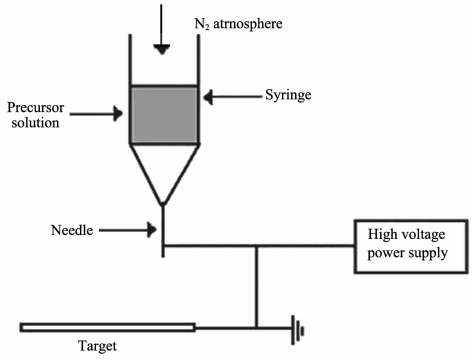


Fig.1　Schematics of the electrospinning apparatus

this synthesis system, the sols were pressurized by own gravity and viscosity. During the electrospinning, the applied voltage was kept at 20 kV and the distance between spinneret and collector was optimized and around 20 cm. The temperature was maintained at 25 ℃. When the spinning was completed, the as-prepared nanofibers were dried in air at 80 ℃ for 72 h.

1.3 Transformation of the gel fibers

All gel fibers dried in air were put into an air-atmosphere programmable tube furnace for heat treatment. The fibers were fired from room temperature to 500 ℃ at a rate of 0.5 ℃·min^{-1} and kept for 1 h and then fired to the desired temperature at 10 ℃·min^{-1} with a hold time of 2 h. The products were naturally cooled to room temperature in the furnace to obtain the desired $MgNb_2O_6$ fibers.

1.4 Characterization

The phase of the $MgNb_2O_6$ fibers was recorded by X-ray diffraction analysis (XRD) using an X-ray diffractometer (Rigaku D/Max 2200PC) with a graphite monochromater and Cu $K\alpha$ radiation (λ=0.151 48 nm) in the 2θ range of 20°~70° at room temperature while the voltage and current were held at 40 kV and 20 mA. Thermal gravimetric analysis (TGA) at an O_2 flow rate of 20 mL·min^{-1} with a heating rate of 10 ℃·min^{-1} was employed to measure the weight loss of gel fibers using a thermal analyzer (TGA/SDTA 851e Mettler). The purity of O_2 was 99.5%. The hollow structure and the diameter of the fibers were observed using a scanning electron microscope (SEM, Hitachi S-520). IR spectra were recorded from 400~4 000 cm^{-1} using a Fourier Transform Infrared spectrophotometer (Nicolet, 5DXFTIR), where the fibers were ground into fine powders, diluted with KBr pellets (the mass percent of KBr was 99%) and pressed into a pellet (the pressure applied was 15 MPa).

2 Results and discussion

The TGA curve of the $MgNb_2O_6$ precursor gel fibers is shown in Fig.2. There is about 14.6% weight loss in the temperature range from room temperature to 120 ℃ on the TG curve of the xerogel fibers due to the removal of water and free organics. In the range 370~500 ℃, there exists a marked weight loss at this temperature range corresponding to the thermal decomposition of the organic ligands. Above 500 ℃, no significant weight loss is observed, which demonstrates that the gel fiber is transformed into an inorganic one indicating the minimum firing temperature to get MgO-Nb_2O_5 compounds in good agreement with the XRD result. The weight percentage for the solid of the gel fibers is about 9% and the formation of hollow structure may be relative to the low weight percent solid on a large degree.

The morphologies of precursor gel fibers and $MgNb_2O_6$ ceramic hollow fibers sintered at 900 ℃ for 2 h are characterized by SEM and TEM as shown in Fig.3.

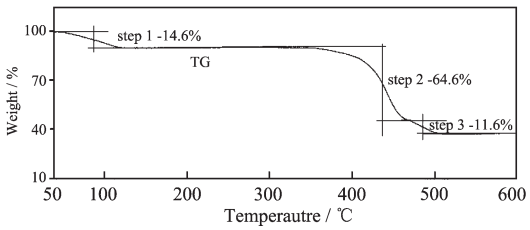


Fig.2 TG curve of $MgNb_2O_6$ gel fibers

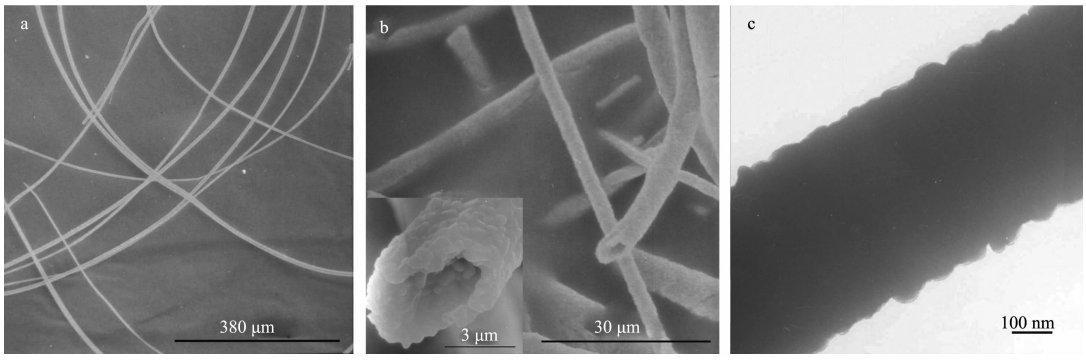
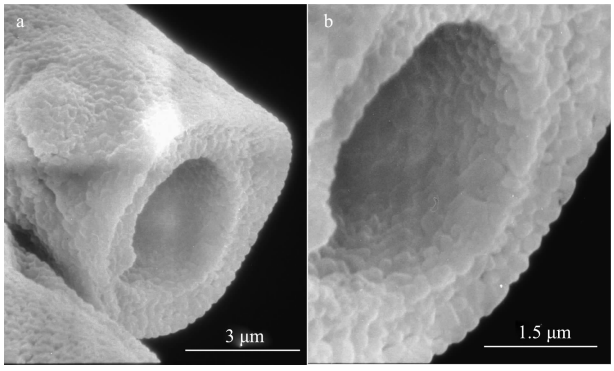


Fig.3 SEM images of (a) precursor gel fibers; (b) $MgNb_2O_6$ ceramic hollow fibers sintered at 900 ℃ for 2 h; (c) TEM image of $MgNb_2O_6$ ceramic fibers sintered at 900 ℃ for 2 h

From Fig.3 (a) it can be seen that precursor gel fibers are continuous and uniform in diameter with a smooth surface. After calcined at 900 ℃ for 2 h, $MgNb_2O_6$ hollow fibers ca. 10 cm in length are still continuous and thin enough to behave flexibly and appear as the dense surfaces and hollow cross-sections (seen in Fig. 3b). The surface of $MgNb_2O_6$ hollow fibers is still smooth and no cracks or splits are observed. The diameter of the thinner hollow fibers is about 400 nm. The fine fibers can also be manipulated on a large scale without the risk of breakage. It has been reported that by minimizing the thickness of the fibers, the tensile and compressive stresses may also be minimized[2]. So, it is expected that as the fiber becomes thinner, it becomes more elastic. The TEM image of $MgNb_2O_6$ fibers indicates that the ceramic hollow fiber is dense and composed of <100 nm nanoparticles.

As can be seen in Fig.4, the cross-section of the $MgNb_2O_6$ fibers is of well-developed tubular morphology. The fiber is uniform along the axis, and the thickness of the wall is no more than 800 nm. The wall of hollow fibers is composed of homogeneous nanoparticles with a particle size of less than 100 nm.



(a) low magnification; (b) high magnification

Fig.4 SEM images of the cross-section of $MgNb_2O_6$ ceramic hollow fibers

According to the TGA results, the precursor gel fibers are heat-treated in the temperature-programmed tube furnace under air atmosphere, and the formation of $MgNb_2O_6$ ceramic fibers is detected by means of IR and XRD. Fig.5 shows the IR spectra of the gel fibers and $MgNb_2O_6$ ceramic fibers sintered at 800 ℃. As shown in Fig.5a, the strong band at 3 440 cm^{-1} is assigned to the hydroxyl stretching mode $\nu_{(OH)}$. This band has been

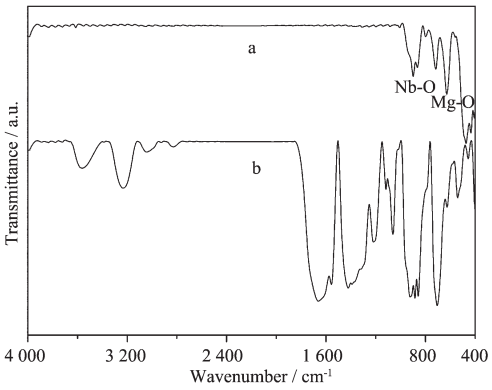
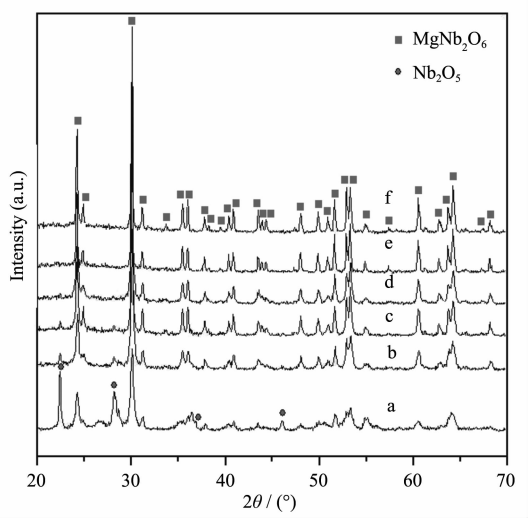


Fig.5 FTIR spectra of (a) the uncalcined $MgNb_2O_6$ precursor fibers; (b) $MgNb_2O_6$ precursor fibers calcined 800 ℃ for 2 h

broadened at 3 200~3 600 cm^{-1} which confirms that citrate is coordinated to Nb ions. The two bands at 2 940 and 2 850 cm^{-1} are attributed to the stretching vibration of CH ($\nu_{(CH)}$). The two characteristic absorption peaks of carbonyl group of citric acid at 1 700 and 1 760 cm^{-1} move to lower wave number due to t he coordination to metal ions which gives rise to the asymmetric and symmetric carbonyl vibration peaks at 1 600 and 1 399 cm^{-1}, respectively[10]. The IR spectrum of $MgNb_2O_6$ ceramic hollow fibers calcined at 800 ℃ for 2 h is shown in Fig.5b. In the low-energy region of the spectrum, the bands at 897, 795 and 722 cm^{-1} are ascribed to the characteristic vibration of Nb-O. In the low-energy region of the spectrum, the bands at 400~600 cm^{-1} are assigned to the characteristic vibration of Mg-O. The FTIR spectra results indicate that $MgNb_2O_6$ has been formed in the powder calcined at 800 ℃, in good agreement with the TGA determined previously.

The XRD patterns of the fibers are shown in Fig.6. Obviously, $MgNb_2O_6$ is the main phase at 600 ℃ and a small quantity of Nb_2O_5 phase coexists. The pure $MgNb_2O_6$ can be obtained at the temperature of 900 ℃. All the d-lines of these reflections match with those of $MgNb_2O_6$ in PDF file No. 33-0875. This proves that the columbite phase $MgNb_2O_6$ ceramic fibers prepared by the sol-gel process could be formed under the low sintering temperature. According to Scherer equation, the FWHM of the XRD patterns of the $MgNb_2O_6$ hollow fibers decreases with increasing temperature due to



(a) 600 ℃; (b) 700 ℃; (c) 800 ℃; (d) 900 ℃; (e) 1 000 ℃ and (f) 1 100 ℃

Fig.6 XRD patterns of $MgNb_2O_6$ ceramics fibers sintered at different temperatures for 2 h

grain growth. Based on the above results, it is concluded that no intermediate phase is formed and the single $MgNb_2O_6$ phase is observed at 900 ℃.

3 Conclusions

In conclusion, $MgNb_2O_6$ hollow fibers were prepared by electrospinning combined with sol-gel process and citric acid was used as a chelating reagent. The calcined $MgNb_2O_6$ hollow fibers are composed of nanoparticles and the thickness of the wall is no more than 800 nm.

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