RAPID SYNTHESIS OF NANOCRYSTALLINE $Bi_4Ti_3O_{12}$ BY CHEMICAL SOLUTION DECOMPOSITION TECHNIQUE *

WANG Shao-Wei[1,2] LU Wei[1)] WANG Hong[2)] WANG Min[2)] SHI Guo-Liang[1)]
LI Ning[1)] LI Zhi-Feng[1)] CHEN Xiao-Shuang[1)] SHEN Xue-Chu[1)]
([1)]National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China;
[2)]State key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong 250100, China)

Abstract By using $Bi(NO_3)_3 \cdot 5H_2O$ and $Ti(OC_4H_9)_4$ as raw materials nanocrystalline $Bi_4Ti_3O_{12}$ was successfully synthesized by chemical solution decomposition (CSD) technique. The nanocrystallite was preliminarily studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Based on the anthors' investigations, the layered structure of $Bi_4Ti_3O_{12}$ was observed, and it was found that nanocrystalline $Bi_4Ti_3O_{12}$ has club-shaped structure.

Key words nanocrystalline materials, $Bi_4Ti_3O_{12}$, CSD technique.

化学溶液分解法快速合成 $Bi_4Ti_3O_{12}$ 纳米晶材料

王少伟[1,2)] 陆 卫[1)] 王 弘[2)] 王 民[2)] 史国良[1)] 李 宁[1)] 李志峰[1)] 陈效双[1)] 沈学础[1)]
([1)]中国科学院上海技术物理研究所红外物理国家重点实验室，上海，200083；
[2)]山东大学晶体材料国家重点实验室，山东，济南，250100)

摘要 以 $Bi(NO_3)_3 \cdot 5H_2O$ 和 $Ti(OC_4H_9)_4$ 为原料，采用化学溶液分解法(CSD)成功地合成了 $Bi_4Ti_3O_{12}$ 纳米晶体材料. 这些纳米晶经过X-射线衍射(XRD)和透射电子显微镜(TEM)的初步研究，观察到了层状结构的 $Bi_4Ti_3O_{12}$，并发现了 $Bi_4Ti_3O_{12}$ 纳米晶体具有棒状结构.

关键词 纳米材料，$Bi_4Ti_3O_{12}$，CSD法.

Introduction

Nanometer-sized crystals and, nanotubes in especially[1-3], have attracted much attention because of their size and their predicted structure-sensitive properties[4,5]. Bismuth titanate ($Bi_4Ti_3O_{12}$) is a typical ferroelectric material with a layered perovskite structure[6-8]. It has a low dielectric permittivity, high Curie temperature, and large spontaneous polarization, making it receive wide applications, either in ceramics (capacitors, sensors, etc.), or in films, such as electro-optic devices and nonvolatile ferroelectric memories[6,9,10]. The $Bi_4Ti_3O_{12}$ thin films have been prepared by a variety of methods, such as radio-frequency (rf) sputtering[11], MOCVD[12], pulsed laser deposition[13] and Sol-Gel[7,14,15]. Yet, very few reports exist on the preparation of nanocrystalline $Bi_4Ti_3O_{12}$ by wet chemical methods such as chemical coprecipitation[6] and Sol-Gel[8]. It is time-consuming to prepare $Bi_4Ti_3O_{12}$ ultrafine powders by Sol-Gel

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since it takes about twenty-three days to do so[8]. However, it takes only several hours to prepare $Bi_4Ti_3O_{12}$ ultrafine powders by chemical solution decomposition (CSD) technique. CSD is a technique especially useful for simplifying processes, reducing processing costs and stochiometric composition control. In our previous work, CSD technique has been successfully used to prepare different kinds of thin films[16~20]. In this paper we present the results of preparation and microstructure of nanocrystalline $Bi_4Ti_3O_{12}$ by CSD technique.

1 Experimental procedure

We used bismuth nitrate[$Bi(NO_3)_3 \cdot 5H_2O$] and butoxide[$Ti(OC_4H_9)_4$] as raw materials to prepare nanocrystalline $Bi_4Ti_3O_{12}$. Bismuth nitrate was initially dissolved in 2-methoxyethanol. Some of the solvent reacted with $Bi(NO_3)_3$ to yield bismuth complex as follows:

$$Bi^{3+} + 4CH_3OCH_2CH_2OH \rightarrow [Bi(CH_3OCH_2CH_2OH)_4]^{3+}$$

The formation of $[Bi(CH_3OCH_2CH_2OH)_4]^{3+}$ prevents the hydrolysis of Bi^{3+} from yielding a white precipitate $BiONO_3$:

$$Bi^{3+} + NO_3^- + H_2O \rightarrow BiONO_3 \downarrow + 2H^+$$

Then titanium butoxide was added to the solution in a molar ratio of Bi:Ti of 4:3 and subsequently polymerized to form a three-dimensional network

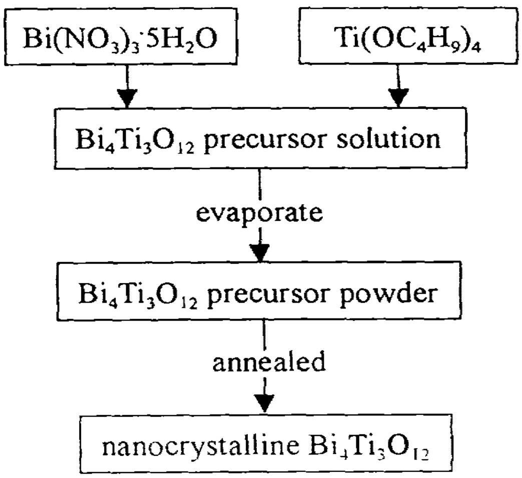

Fig. 1 The flow chart for synthesizing nanocrystalline $Bi_4Ti_3O_{12}$ by the CSD technique

图 1 CSD技术合成$Bi_4Ti_3O_{12}$纳米晶材料流程图

structure[21]. The resultant solution was stirred to be homogeneous[16~19]. It was heated to evaporate the solvent to form $Bi_4Ti_3O_{12}$ precursor powder. And the powder samples were annealed to burn off the residual organics and form crystalline $Bi_4Ti_3O_{12}$:

$$2Bi_2O_3 + 3TiO_2 \rightarrow Bi_4Ti_3O_{12}$$

All the process was completed in two hours. CSD is a time-saving way for preparing nanocrystalline materials. The flow chart for preparing nanocrystalline $Bi_4Ti_3O_{12}$ by the CSD technique was shown in Fig. 1.

2 Results and discussion

In order to investigate the phase structure of $Bi_4Ti_3O_{12}$ in powder, the powder samples were characterized by a Rigaku D/MAX-γA X-ray diffractometer. Fig. 2 shows the XRD pattern of $Bi_4Ti_3O_{12}$ powder annealed at 650 ℃ for 2 min. The interplanar spacing (d) values of the peaks agree with those of $Bi_4Ti_3O_{12}$ given in the JCPDS data cards, indicating that the powder is crystalline $Bi_4Ti_3O_{12}$.

The microstructure of the crystalline $Bi_4Ti_3O_{12}$ was studied by a Joel-100CX TEM (made in Japan). Fig. 3(a) shows the particles of $Bi_4Ti_3O_{12}$, the same as the particles reported in Ref[8]. The average size of the particles shown in Fig. 3(a) is about 50 nm. We observed sheets of the crystalline $Bi_4Ti_3O_{12}$ at the same time[shown in Figs. 3(a)~3(c)]. It is consistent with the layered structure of $Bi_4Ti_3O_{12}$ crystal presented in Refs[6~8]. To our surprise, we observed club-shaped $Bi_4Ti_3O_{12}$ as well. Fig. 3(e)

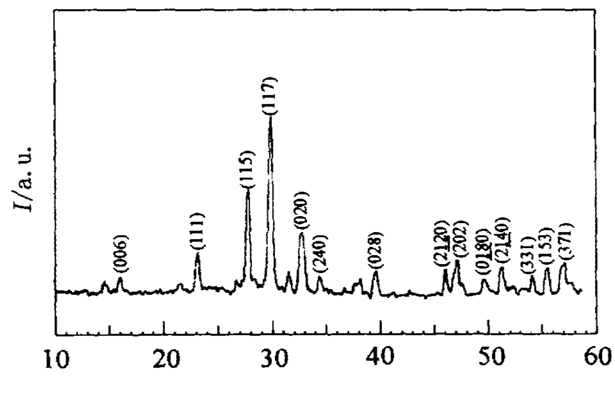

Fig. 2 XRD pattern of $Bi_4Ti_3O_{12}$ powder annealed at 650 ℃ for 2 min

图 2 650 ℃退火 2 min后$Bi_4Ti_3O_{12}$粉末的XRD谱图

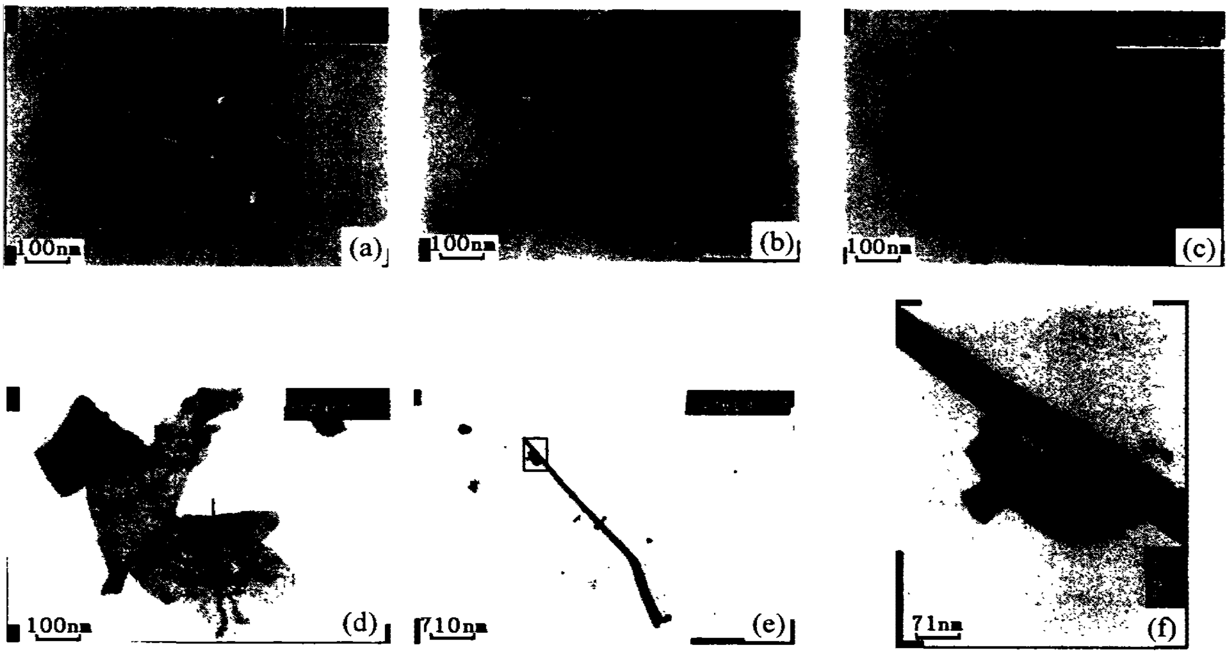

Fig.3 TEM photographs of $Bi_4Ti_3O_{12}$ powder
图 3 $Bi_4Ti_3O_{12}$粉末的 TEM 照片

shows one of them. The thin tip of the club is 60 nm in width and the fat one is 190 nm in width. The club is 3900 nm long. Fig. 3(f) is the photograph of the thin tip being magnified 10 times. How did the club-shaped $Bi_4Ti_3O_{12}$ form?

From the photographs, we can find easily that there are several stripes on each sheet. They are curved extinctive stripes that vary with the change of the angle between the sample and the incident electronic beam[22]. We took photos before and after moving the sheets to see if there were any changes to occur. Arrows point out three of the stripes on a sheet[shown in Fig.3(c)]before it was moved, while Fig.3(d) shows the photograph of the sheet after it was moved. The shapes of the stripes changed apparently after the sheet had been moved and, even more, one of the stripes disappeared. There are apparent differences between the two photographs, indicating that the stripes are really curved extinctive stripes and the sheets are curved sheets. Therefore, it is possible that the sheets curl up to be clubs in certain annealing condition. One possible formation mechanism of club-shaped $Bi_4Ti_3O_{12}$ is that sheet-like $Bi_4Ti_3O_{12}$ initially forms and then curls up to be club-shaped $Bi_4Ti_3O_{12}$ under the thermal field. Is the club-shaped $Bi_4Ti_3O_{12}$ solid or not? Has it any attractive structure-sensitive properties? These problems are under our investigation.

3 Summary

Nanocrystalline $Bi_4Ti_3O_{12}$ was synthesized by the CSD technique. Based on our investigations. we have found for the first time that nanocrystalline $Bi_4Ti_3O_{12}$ has club-shaped structure. One possible formation mechanism of the structure is that the sheet initially forms and then curls up to be club in certain annealing condition.

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