

# Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles prepared by hydrothermal synthesis

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## Abstract

The influence of hydrothermal conditions (including starting materials, reaction temperature and time) on the crystal structure and the morphology of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles are discussed in this paper. Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanocrystalline particles were hydrothermally synthesized at temperatures in the range of 180–230 °C for 4–12 h, from Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, TiCl<sub>4</sub> and NaOH solution. The XRD results revealed that a typical bismuth layered perovskite structure Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> was obtained. The TEM showed that the Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles are tabular, and the sizes are about 200 nm. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>; Ferroelectric properties; Hydrothermal synthesis; Nanoparticles

## 1. Introduction

Bismuth titanate (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) has a layered perovskite structure, built up by the regular intergrowth of [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> layer and perovskite type layers [Bi<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> where Bi ions occupy twelve-coordinated sites.<sup>1–3</sup> The compound is monoclinic (C<sub>1h</sub>=m) at room temperature, and then turns into tetragonal (D<sub>4h</sub>=4 mmm) above the Curie temperature (675 °C).<sup>4</sup> As a typical ferroelectric, piezoelectric and electro-optic material, having relatively low coercive field, low dielectric constant, high Curie temperature and high breakdown strength,<sup>5–7</sup> Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> exhibits potential use in applications such as non-volatile memory, optical memory, piezoelectric and electro-optic devices.

It is well known that the morphology and compositional homogeneity of the powders greatly influence the electrical properties of the ceramics. For example, Villegas et al.<sup>8</sup> found that the higher dielectric constant, Curie temperature and electromechanical response of Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-based ceramics were due to the high compositional homogeneity in the reaction sintering processing, compared with conventional solid-state

method. Usually, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> is prepared by conventional solid-state reaction which often results in high agglomeration and compositional inhomogeneity of powders because of high calcination temperature and repeated grinding.<sup>9</sup> Several alternative chemical synthesis routes have been proposed including hydrolysis of metal organic salts,<sup>10</sup> co-precipitation method,<sup>11</sup> sol-gel process<sup>12</sup> and so on. However, a high sintering temperature is usually necessary for the crystallization of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> powders, although the improved chemical methods can produce fine powders with compositional homogeneity. As a method for synthesizing high quality powders that have many advantages, such as high degree of crystallinity, well-controlled morphology, high purity and narrow particle size distribution,<sup>13,14</sup> hydrothermal synthesis was regarded as a promising way to prepare bismuth titanate powders. Until now, several papers have been reported to successfully synthesize bismuth titanate powders by hydrothermal processes, but some limited results were obtained, and hydrothermal synthesis conditions need to be optimized further.<sup>15,16</sup> There has been no report on hydrothermal synthesis of quadrature bismuth titanate nanoparticles. Therefore, in this paper, the influence of the starting materials, reaction temperature and time on the crystal structure and the morphology of bismuth titanate by hydrothermal synthesis were investigated.

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Chemically homogeneous and dense ceramics resulting from the hydrothermal nanoparticles can be obtained at lower temperatures, and they have comparable dielectric and piezoelectric properties with the best ceramics prepared by the conventional processing. In addition, The high performance ceramics with grain orientation can be fabricated by the platelet morphology of bismuth titanate, which make it possible to obtain polycrystalline ceramics with properties similar to those of single crystals along some crystal axes.

## 2. Experimental

### 2.1. Hydrothermal synthesis of nanoparticles

The starting materials for the hydrothermal synthesis may be all kinds of compounds that can be dissolved in water under high-temperature and high-pressure. In this experiment, titanium butoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ), titanium chloride ( $\text{TiCl}_4$ ) and anatase titania ( $\text{TiO}_2$ ) powder were used as titanium salts; bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) and bismuth hydroxide ( $\text{Bi}(\text{OH})_3$ ) were used as bismuth salts. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were used as mineralizers. All the chemical reagents were of analytical grade. The hydrothermal synthesis of bismuth titanate was conducted in a Teflon-lined stainless steel autoclave with a filling capacity of 80%. The hydrothermal process of bismuth titanate is shown in Fig. 1.

### 2.2. Microstructure characterizations

The phase structure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanoparticles was analyzed by an X-ray diffractometer (XRD) using a  $\text{CuK}\alpha_2$  radiation at 40 kV and 60 mA with a nickel filter and a graphite monochromator (Rigaku D/max-rB). The mean grain size and morphology of the synthesized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  particles were observed by a Transmission Electron Microscopy (JEM-200CX TEM), whose operation voltage is 120 kV. All the samples were analyzed at room temperature. Differential thermal analysis (DTA) of the bismuth titanate particles was carried out with a Shimadzu TGA-50H simultaneous thermal analyzer.

## 3. Results and discussion

### 3.1. The influence of the starting materials

The inherent characteristics of precursors always determine chemical reaction between different materials, so the optimal combination of different starting materials is essential to hydrothermally synthesize high quality  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  particles.

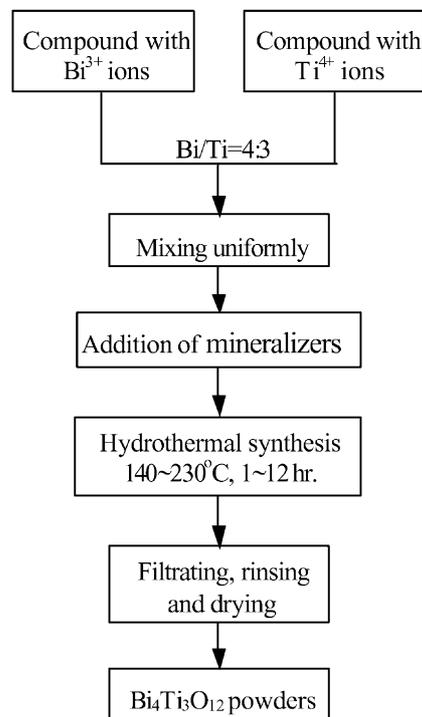


Fig. 1. Flow chart of the hydrothermal process.

Different starting materials were combined between compounds with  $\text{Bi}^{3+}$  and compounds with  $\text{Ti}^{4+}$ . Amorphous  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$  is prepared through hydrolyzing, filtrating, rinsing and drying of titanium butoxide. The starting materials were hydrothermally treated at a ratio of  $\text{Bi}:\text{Ti}=4:3$  under various hydrothermal conditions which were summarized in Table 1. It can be seen that the crystal structure of bismuth titanate is strongly dependent on starting materials. Pure  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  can be obtained when any of three combinations were used as for samples No. 1, No. 4 and No. 5, which demonstrated that the compounds of  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ ,  $\text{TiCl}_4$ ,  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$  and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  had higher reactivity than the compounds of  $\text{TiO}_2$  and  $\text{Bi}(\text{OH})_3$ . The bismuth and titanium compounds mixed homogeneously in the precursors and had a shorter diffusion route to form  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  structure.<sup>17</sup> In addition, the higher alkali concentration also can facilitate the chemical reaction. However, with the starting materials  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ , it is difficult to prepare pure  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  by altering reaction temperature and time, because  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$  was a deoxidant, and can deoxidize  $\text{Bi}^{3+}$  into Bi under high temperature and high pressure system. Therefore, the experiments in the following discussion were carried out using  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{TiCl}_4$  as the starting materials unless otherwise mentioned.

### 3.2. The influence of reaction temperature and time

Using  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{TiCl}_4$  at the mole ratio 4:3, the hydrothermal synthesis of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powder was

Table 1  
The influences of hydrothermal synthesis conditions on the crystal structure of the products

Starting materials	No.	Mineralizer (M)	Temperature (°C)	Time (h)	Crystal structure
Ti(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub>	1	KOH = 0.5	220	20	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> + Bi
Ti(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub>	1	KOH = 0.5	220	40	Bi
Ti(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub>	1	KOH = 0.5	240	14	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>
Ti(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub>	2	KOH = 0.5	220	72	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> + X <sup>c</sup>
TiO <sub>2</sub> <sup>a</sup>	3	KOH = 0.5	240	14	Bi <sub>2</sub> TiO <sub>20</sub> + X
TiCl <sub>4</sub>	4	NaOH = 3.0	210	6	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>
TiO <sub>2</sub> ·nH <sub>2</sub> O <sup>b</sup>	5	NaOH = 3.0	230	12	Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>
TiO <sub>2</sub>	6	NaOH = 3.0	230	12	Bi <sub>2</sub> TiO <sub>20</sub> + Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub>

<sup>a</sup> Anatase TiO<sub>2</sub>.

<sup>b</sup> Amorphous.

<sup>c</sup> Unknown phase.

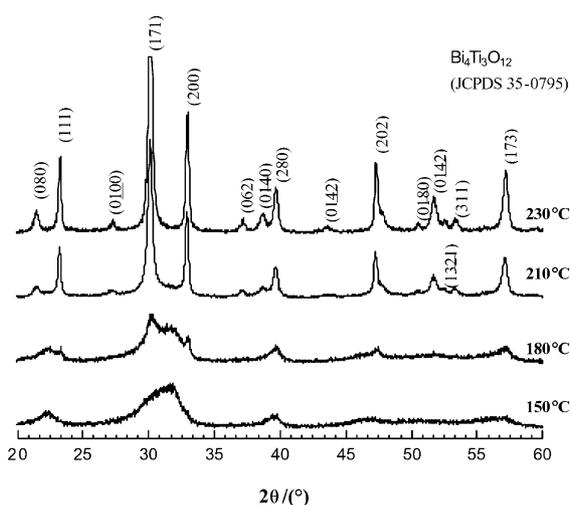


Fig. 2. The XRD patterns of powders synthesized at different temperatures for 6 h.

carried out in a 3M NaOH aqueous solution at temperatures of 150, 180, 210 and 230 °C. The XRD patterns of prepared particles are shown in Fig. 2. After heating at 150 °C for 6 h, two small diffraction peaks of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, indexed as (280) and (173), were observed. With an increase of the reaction temperature, the diffraction peaks of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> became clear. When reaction temperature increased to 230 °C, the heights of the diffraction peaks belonging to Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> increased further, while full-width at half-maximum of all peaks decreased. It revealed that bismuth titanate particles with well-crystallinity were synthesized at higher temperature. All diffraction peaks are assigned to Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> as reported in JCPDS file,<sup>18</sup> indicating that the synthesized particles were monophasic bismuth titanate. Compared with the previous solution process,<sup>10</sup> the hydrothermal process developed herein successfully decreased the synthesis temperature of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> from 550 to 210 °C. It is evident that the hydrothermal environment remarkably accelerates the reaction kinetics of the formation of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>.

Table 2

The specific surface of powders hydrothermally prepared under different temperature and time

Reaction temperature (°C)	180	210	230	230	230
Reaction time (h)	6	6	2	6	12
Specific surface (m <sup>2</sup> g <sup>-1</sup> )	32.7	29.35	31.99	29.71	15.3

In order to understand the influences of reaction time on the synthesis of bismuth titanate, the reaction temperature was fixed at 230 °C, and the reaction time was prolonged from 1 h to 12 h. Fig. 3 shows the XRD patterns of hydrothermal synthesized Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles at various reaction time. It was found that Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> crystallites began to be formed at 1 h, and the peak intensity of obtained particles tends to increase with increasing of reaction time. It revealed that well crystallized Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles can be synthesized between 4 h and 12 h (Fig. 3).

As well known, particle size can be expressed by the specific surface area, i.e. BET value. The specific surface area of bismuth titanate powders decreased with rising reaction temperature and time, as can be seen in Table 2. It is shown that the particle sizes of bismuth titanate powders increased with rising the reaction temperature or prolonging the reaction time.

In conclusion, it was found that increasing both reaction temperature and time had a positive effect on the formation of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>. When reaction temperature was too low, hydrothermal reaction didn't take place and the powders were amorphous; Similarly, it was difficult to obtain good crystalline Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> for shorter reaction time, because of inadequacy of hydrothermal reaction. The XRD results showed that pure bismuth titanate powders can be obtained, while reaction temperature was higher than 210 °C for 6 h, or reaction time was longer than 4 h at 230 °C. The crystallinity of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles were improved with rising reaction temperature and time.

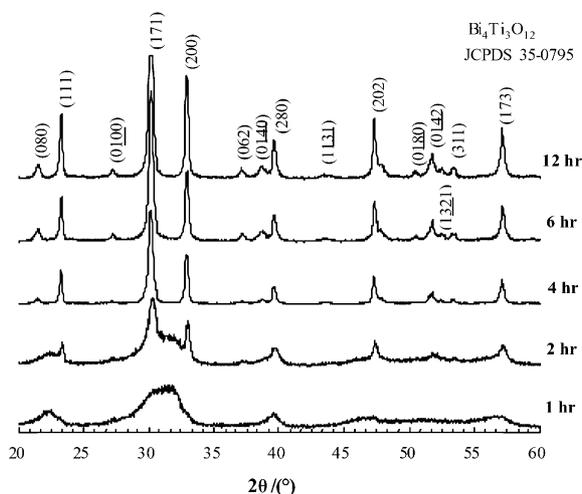


Fig. 3. The XRD patterns of products synthesized hydrothermally at 230 °C for different reaction time.

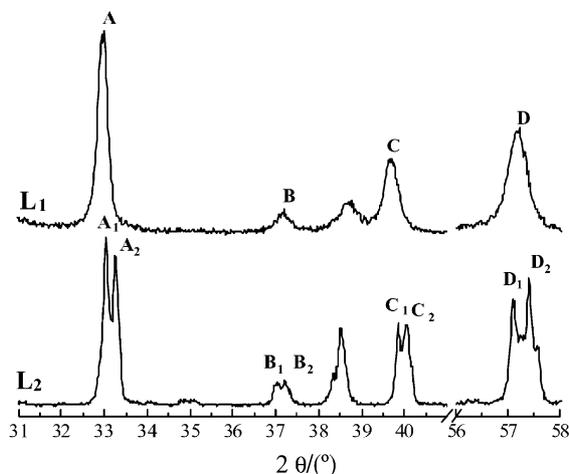


Fig. 4. XRD patterns of the tetragonal phase (L<sub>1</sub>: hydrothermal Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> powders) and peak splitted of the orthorhombic phase (L<sub>2</sub>: solid-state Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> powders). The splitting peaks are at 2.71 Å (A), 2.41 Å (B), 2.27 Å (C), and 1.61 Å (D).

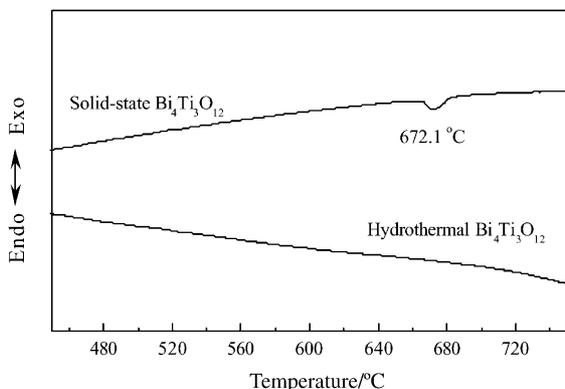


Fig. 5. DTA curves of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles, prepared by hydrothermal and solid-state reaction.

To distinguish between the tetragonal and orthorhombic phase structures of obtained Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles, the XRD patterns were compared with that of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles prepared by solid-state method. As seen from Fig. 4, peak splitting occurred at  $d$  near 2.71, 2.41, 2.27 and 1.61 Å, which is a characteristic indication of the orthorhombic phase,<sup>3</sup> while such phenomena didn't appear in the hydrothermal bismuth titanate powders. Since there is a orthorhombic-tetragonal phase transition of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> crystals around the Curie point at 675 °C, an endothermic peak in DTA curves is expected while heating solid-state Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles. However, if the hydrothermally synthesized Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles are tetragonal, there will be no phase transition and no endothermic peak around 675 °C. Fig. 5. shows the DTA results of hydrothermal and solid-state Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles. As one can expect, there is no endothermic peak between 450 and 750 °C. The absence of the enthalpy peak around the Curie point indicates no phase transition around 675 °C. In contrast, there is an endothermic peak in orthorhombic Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> particles. Therefore the hydrothermal bismuth titanate powders belonged to tetragonal structure. This can be conformed also from TEM micrograph and corresponding electron diffraction patterns of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> powders obtained as seen in Fig. 7.

### 3.3. TEM observation of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles

The TEM micrograph and EDS spectra of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles hydrothermally synthesized at 230 °C for 6 h are presented in Fig. 6. As seen in Fig. 6(a), the as-prepared powders were non-agglomerated nanoparticles, and exhibited both of the tabular and elongated shapes. The sizes of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles are in the ranges of 80–250 nm. The average of size is about 200 nm. The energy dispersive spectroscopy (EDS) was used to investigate particle composition of two kinds of particles. The resolution of EDS is about 10–15 nm. Spectrum A is for the elongated particle, and spectrum B is for the tabular particle. The EDS indicates that they have the same elements and atom percentages [Fig. 6(b)].

The crystal structure of bismuth titanate can be described as a sequence of alternating bismuth oxide and perovskite-like layers stacked along the  $c$ -axis. The two layer are linked by the bond between a Bi ion in the BiO layer and an apex oxygen in the perovskite-like layer. This bond is the weakest in the lattice. The surface energy of (010) is lowered obviously by chloride ion.<sup>19</sup> Under the hydrothermal homogeneous system, the two factors make the growth rate of  $a$  axis and  $c$  axis much faster than that of  $b$  axis, resulting in a platelet morphology with platelet faces composed of (010) planes (as seen in Fig. 7). Calculated from Scherrer's formula of  $D = (k\lambda)/(\beta_{(hkl)}\cos\theta)$ , the sizes of (010) planes, i.e.  $D_{(010)}$ , are about 6.1 nm. Observed from

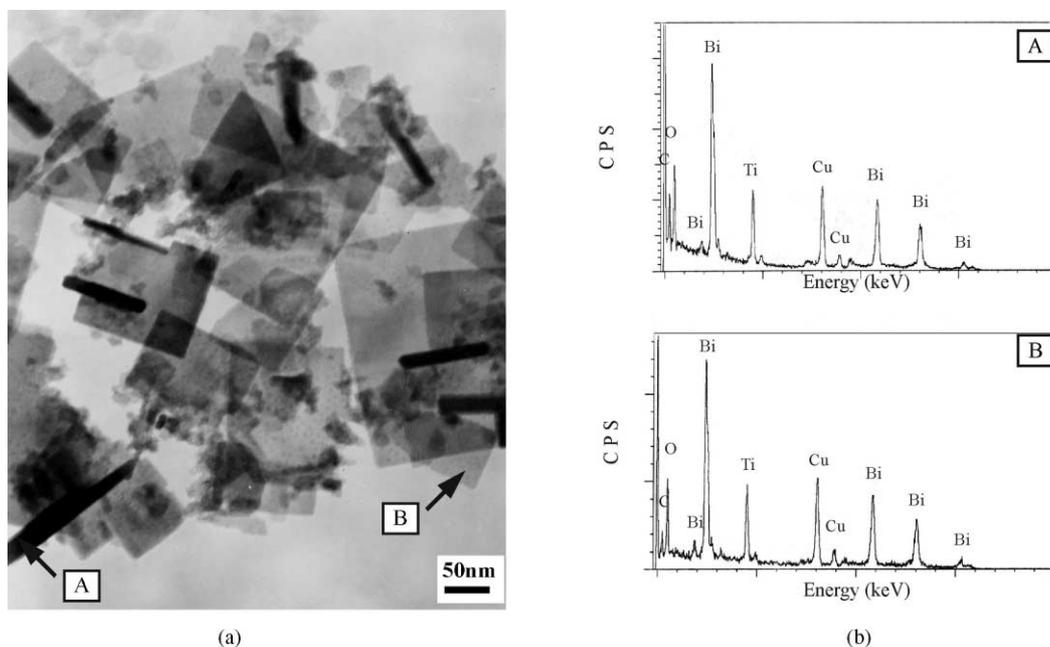


Fig. 6. The TEM photograph and EDS spectra of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders hydrothermally synthesized at  $230^\circ\text{C}$ , for 6 h: (a) TEM photograph; (b) EDS spectra.

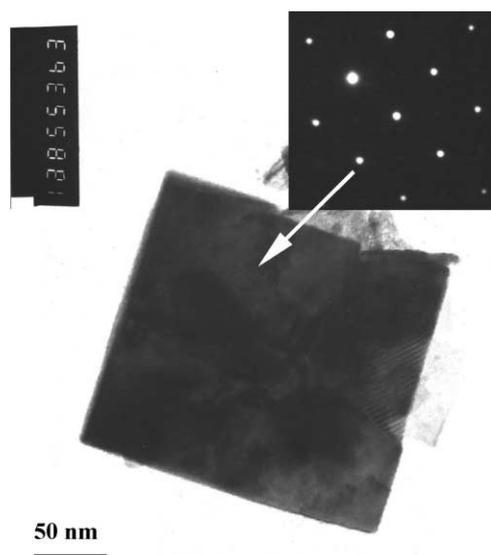


Fig. 7. TEM micrograph and corresponding electron diffraction pattern of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders (3 M NaOH for 6 h at  $230^\circ\text{C}$ ).

HREM, many defects were found in the elongated particles, while such defects were not found in the tabular particles. It is presumed that the growth of some grains were blocked by impurities on some faces, resulting in elongated shapes.

#### 4. Conclusions

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanocrystalline particles were hydrothermally synthesized at temperatures of  $180\text{--}230^\circ\text{C}$ ,

for 4–12 h from  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{TiCl}_4$  and NaOH solution; The crystallinity and the particle sizes of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders were increased with rising reaction temperature and time. The XRD results revealed that a typical bismuth layered perovskite structure  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  was obtained. The TEM showed that the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanoparticles are tabular and the sizes are about 200 nm.

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