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Domain structure of $Bi_4Ti_3O_{12}$ ceramics revealed by chemical etching

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Abstract

Chemical etching of bismuth titanate ($Bi_4Ti_3O_{12}$) ceramics was developed using a mixture of different agents based on HF, NH_4F and H_2O. Thermal etching modifies the surface morphology and this give place to rounded plate-like grains. Suitable etching of $Bi_4Ti_3O_{12}$ samples could be however achieved with chemical agents, because it preserves the original shape of the platelets. Furthermore with this kind of etching two relevant features of the microstructure arise in scanning electron microscopy (SEM) micrographs: the domain structure of the etched grains and the presence of square-shaped holes inside the platelets.

Keywords: Electron microscopy; Platelets; Microstructure-final; $Bi_4Ti_3O_{12}$

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) based materials show a great potential for optical memory, piezoelectric and electro-optic applications.[1,2] $Bi_4Ti_3O_{12}$ (BIT) is a high temperature ferroelectric compound that belongs to the Aurivillius[3] family of bismuth based layered compounds. Its structure can be described as formed by three unit cells of $(BiTiO_3)^{2-}$ with perovskite like structure interleaved with $(Bi_2O_2)^{2+}$ layers. At room temperature it is monoclinic ($c_{1h} = m$) and ferroelectric, but can be represented as orthorhombic with the c-axis normal to the $(Bi_2O_2)^{2+}$ layers.[4] For undoped BIT, ferroelectric to paraelectric transition occurs at 675 °C[5] and the high temperature symmetry is tetragonal ($D_{4h} = 4/mmm$). Spontaneous polarization maximizes in the a–b plane ($P_s \approx 50\ \mu C/cm$)[6] together with the electrical conductivity.[7] Both the relatively high electrical conductivity and the high coercive field observed for these compounds make extremely difficult to polarize polycrystalline BIT-based ceramics in order to obtain an useful piezoelectric response.

BIT-based ceramics microstructure reflects the structural anisotropy showing big platelets-like grains growing preferentially in the a–b plane. Electrical response of these materials is strongly dependent on the microstructure,[8,9] however relevant microstructure features are still poorly known. Reported studies on the microstructure of BIT ceramics are always carried out on polished and thermally etched samples, since successful chemical etching for $Bi_4Ti_3O_{12}$ ceramics has not been reported. Furthermore, experimental difficulties on the sample preparation, have also avoided a meaningful microstructure analysis by TEM.

Very recently, domain structure of Nb-doped $Bi_4Ti_3O_{12}$ ceramics has been revealed by Atomic Force Microscopy on polished and thermally etched samples and discussed in terms of Nb doping and reported data of $Bi_4Ti_3O_{12}$ single crystals.[10] However, thermal etching might induce domain structure changes itself.

In the present paper, a chemical etching method for $Bi_4Ti_3O_{12}$ ceramics is described. Results of the microstructure analysis by Scanning Electron Microscopy are discussed and compared to recently reported data.

2. Experimental procedure

$Bi_4Ti_3O_{12}$ ceramics were prepared by a chemical route, using the hydroxide coprecipitation method. Titanium tetrabutoxide $Ti(C_4H_9O)_4{\cdot}C_4H_9OH$ (Alfa Aesar) and

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$Bi(NO_3)\cdot 5H_2O$ (Riedel de Häen) were used respectively as TiO_2 and Bi_2O_3 precursors. Experimental details are reported elsewhere.[11] BIT powders were uniaxially pressed into disks (115 MPa) and sintered in air at 1000 °C (2 h soaking time).

Table 1
Chemical etching of $Bi_4Ti_3O_{12}$ samples

Solution	Temperature (°C)	Time (s)	Etching effect
	25	60	Negative
	25	90	Low
$HF/NH_4F/H_2O$	25	180	Low
(2:1.2:3)	50	90	Moderate
	50	180	Positive
	50	360	Too high

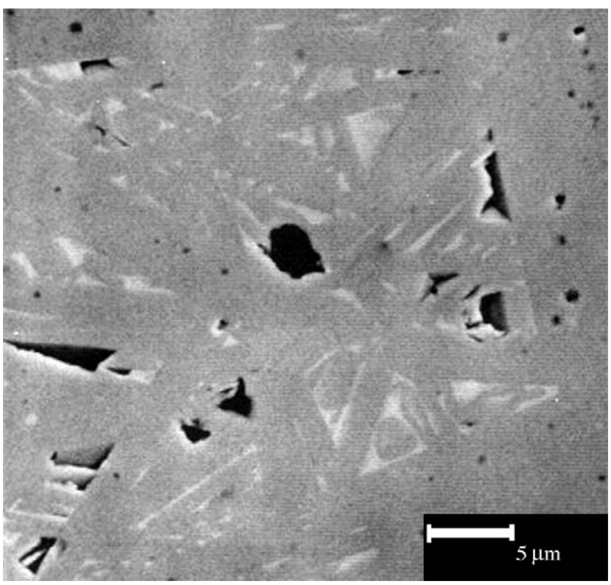

Fig. 1. SEM micrograph of BIT polished surfaces.

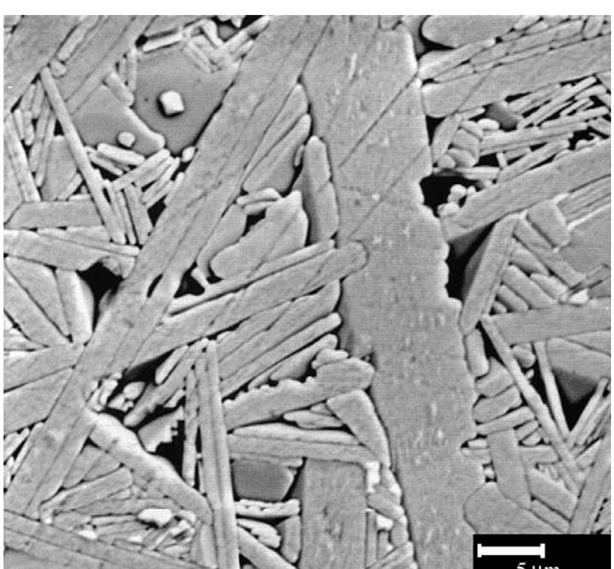

Fig. 2. SEM micrograph of BIT polished and thermally etched surfaces (900 °C for 15 min).

Microstructure analysis was carried by scanning electron microscopy (SEM) (Carl Zeiss DSM 950) on polished and thermally or chemically etched surfaces. Based on reported data on $Bi_2Ti_2O_7$,[12] chemical etching essays were carried out with $HF/NH_4F/H_2O$ (molar ratio 2:1.2:3). Temperature and times analysed are summarized in Table 1. Also, for comparison, thermal etching was done at 900 °C for 1.5 min in certain samples.

3. Results and discussion

Fig. 1 shows a SEM micrograph obtained on the polished surface of the sample sintered at 1000 °C for 2 h. The image has been acquired in the BSE mode. Bright areas

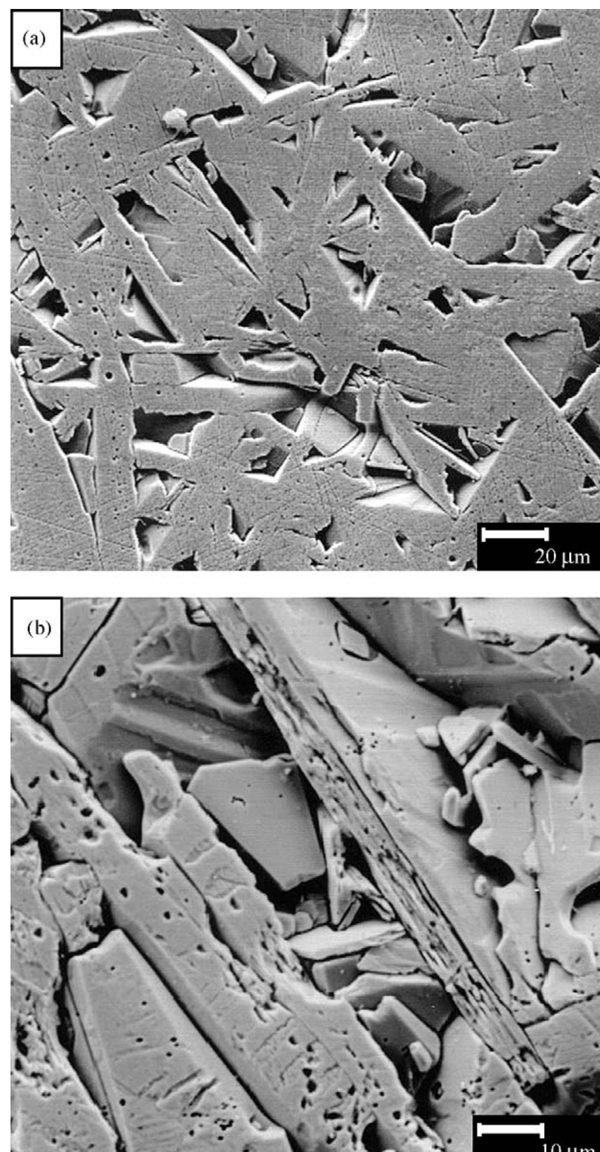

Fig. 3. SEM micrographs of BIT polished and chemically etched surfaces for an etching time of 1.5 min: (a) room temperature and (b) 50 °C.

reflect a bismuth environment of certain regions mainly located between the platelets. Due to the high sintering temperature this phase might appear related to the formation of a Bi_2O_3-rich liquid phase.[13]

Fig. 2 shows typical rounding of plate-like grains, which results from thermal etching. Areas between platelets appear as porous and certain small precipitates are observed on the platelets. This indicates a recrystallization or partial volatilization of the intergranular Bi-rich regions observed in the polished surface of Fig. 1.

When the sample is chemically etched at room temperature for 90 s, (Fig. 3a) the Bi-rich areas are preferentially etched however grain boundaries are not revealed. Further increase of time at room temperature does not improve sample etching.

Increasing temperature up to 50 °C (Fig. 3b) improves etching and now grain boundaries and other structures are clearly observed. Platelets show sharp boundaries instead of the rounded ones observed in the thermally etched samples. Furthermore, small irregular holes appear in the platelets as a consequence of preferential etching. Etching progresses when increasing time (Fig. 4) and reveals two main features: domain structure and square-shaped holes inside the platelets.

Geometrical patterns appeared in samples showed in Fig. 4 coincide with those observed by Zhang et al.[10] Preferential etching on certain crystallographic directions, as observed for other materials like twin boundaries,[14] evidence the domain structures. Both 90° and 180° domain geometries are evidenced in un-doped BIT ceramics,[6,15] however 90° domain walls parallel to the *c*-axis (marked in Fig. 4a) are more frequent than 180° domain walls parallel to a–b plane (marked in Fig. 4b).

Since square-shaped porosity is unlikely to occur, square-shaped holes observed inside the platelets indicate the presence of Bi-rich microregions that are preferentially etched. The origin of these holes could be related to the presence of compositional fluctuations or even $Bi_2Ti_2O_7$ microcrystals[16] whose pyrochlore type structure is consistent with the square shape of the holes. However, further work is needed to clarify this point.

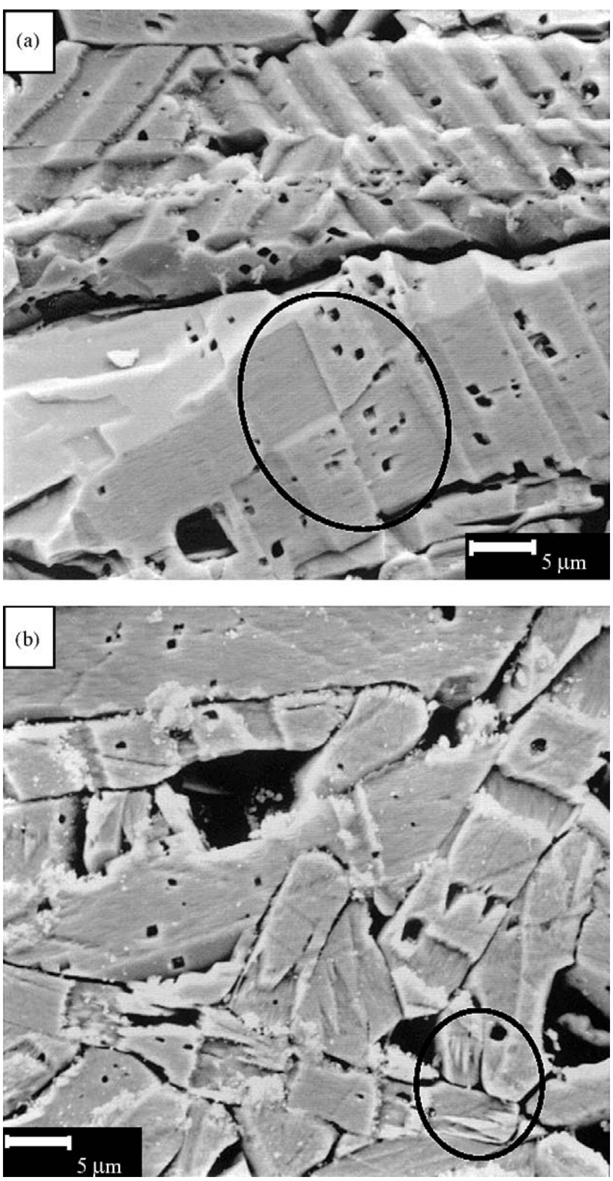

Fig. 4. SEM micrographs of BIT polished and chemically etched surfaces at 50 °C: (a) etching time 3 min. Marked areas show 90° domain walls parallel to the *c*-axis and (b) Etching time 6 min. Marked areas show 180° domain walls parallel to a–b plane.

4. Conclusions

A mixture of HF, NH_4F and H_2O at a molar ratio of 2:1.2:3 was successfully used to chemically etch polished samples of $Bi_4Ti_3O_{12}$. The best etching condition is 50 °C for 3 min. Shape of grains changed from rounding plate-like grains observed at thermally etched samples to platelets under the action of the chemical agent, pointing out that the thermal etching modifies the morphology of the microstructure. The chemical etching shows also the domain structure of the etched grains, which is preferentially observed in the Bi-rich regions. Both 90° and 180° domain geometries are evidenced in un-doped BIT ceramics although 90° domain walls parallel to the *c*-axis are more frequent than 180° domain walls parallel to a–b plane.

Moreover small square holes appear in the platelets as a consequence of preferential etching. The origin of these holes could be related to compositional fluctuations as well as to the presence of a $Bi_2Ti_2O_7$ pyrochlore type secondary phase.

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