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STUDY ON CRYSTAL STRUCTURE OF $PbTiO_3$ NANOWIRES BY X-ray RESEARCHES

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$PbTiO_3$ nanowires is produced by stainless steel reaction kettle with Teflon lined. The crystal structure of nanowire was analyzed by electron backscatter diffraction (EBSD). At present, EBSD is seldom used to analyze these powder materials with fine crystalline grain and nanosized materials. An attempt is carried out to analyze the powder materials with fine crystalline grain by EBSD. $PbTiO_3$ nanowires is investigated by EBSD, and then analyzed by X-ray diffraction and Scanning Electron Microscopy (SEM). The crystal structure of $PbTiO_3$ is P4mm(99), and the cell parameter is cell = 3,905 × 4,156 Å. Experimental results of EBSD are accordant with that of XRD, which illuminates that surface EBSD analysis technique is feasible to determine crystal structure and orientation of powder material with new structure.

Key words: $PbTiO_3$, nanowires, crystal orientation, X-ray researches

INTRODUCTION

High Electron backscattered diffraction (EBSD) based on electron backscattered diffraction patterns is a new microstructure analysis technique applied to scanning electron microscopy (SEM) in the early 1990s[1]. This technology can conduct crystallography analysis point by point on the nanoscale microstructure of the block sample, obtain the crystal orientation map, combine the microstructure and micro area composition on the scanning electron microscope with crystallography or texture analysis, and change the traditional research methods of microstructure and crystallography analysis. This technology has greatly expanded the application range of SEM and has now become a standard attachment for SEM similar to X-ray energy dispersive spectroscopy (EDS).

In recent years, the Electron backscattered diffraction (EBSD) analysis technology has been widely used in the fields of material science, geology, metallurgy, archaeology and other fields, but its research objects are only limited to the range of block materials with good conductivity, and the test research on powder materials with small grains and even nano materials is still blank. At present, EBSD is mainly used for crystal orientation analysis [2]. In terms of structural analysis, phase discrimination methods are still used [3], which first rely on Energy Dispersive Spectroscopy (EDS) to measure the chemical composition of the sample to be analyzed, list possible phases based on the composition, and then attempt to calibrate the EBSD pattern in sequence, using exclusion method to determine the structure of the phase to be analyzed.

$PbTiO_3$ (PT) is an important ferroelectrics with a high Curie Point Temperature of 490 / °C, a tetragonal system of c / a = 1,064 which makes it one of the largest spontaneous polarization among ferroelectric materials and its electronic structure has been studied extensively [4-5]. With the miniaturization of piezoelectronic and electromechanical devices, the requirements for free standing nanostructures that can be applied to these devices keep increasing [6].

This study used a hydrothermal method to prepare lead titanate ($PbTiO_3$) nanowires. EBSD was used to repeatedly test and study the crystal structure. The reliability of the results was verified by XRD method. It is achieved developing the application of EBSD technology in the field of powder crystal materials.

EXPERIMENT

Preparation of $PbTiO_3$ crystals

The hydrothermal reaction of for preparing $PbTiO_3$ nanocrystals in this work was carried out in an autoclave self-made with Teflon (poly-tetrafluoroethylene) lining and stainless steel. Deionized water were used in the preparation of all aqueous solutions. Titanium were added in the form of a precipitated hydroxide $TiO(OH)_2$(TOH). When preparing the precipitated TOH, ammonia was used as precipitant. $(C_4H_9O)_4Ti$ was dissolved in deionized ethanol to form 0,1M Ti^{4+} solution. Subsequently, the precipitated TOH was prepared by introducing the Ti^{4+} solution into a 0,15M am-

J. B. Liu , J. Wang (corresponding author, wj_sisi@163.com). School of Application Technology College, University of Science and Technology LiaoNing , Anshan 310044 , China.

monia solution under stirring condition. For eliminating ammonium ions, the TOH precipitate was filtered and washed with deionized water for six times. The fresh TOH precipitate was then re dispersed in deionized water under vigorous stirring, followed by

$Pb(NO_3)_2$, KOH pellets and polymer solution addition. In the final suspension, a TOH concentration of 0,1M, a KOH concentration of 2M and PVA concentration of 0,8 $g \cdot L^{-1}$ were designed respectively. The amount of PAA introduced was designed to the amount of PVA introduced in weight ratio of 12,5 : 1 and 10 : 1 for PEG. The feedstock prepared above was charged into a 50 ml stainless-steel Teflon-lined autoclave. The hydrothermal treatment was performed by putting the autoclave into an oven and kept at 200 / °C, and then cooled to room temperature in air naturally.

The sample in this work was prepared with Pb / Ti = 1 and 24 / h reaction processing.

Figure 1 is the SEM picture of $PbTiO_3$ nanowires. $PbTiO_3$ powders is light yellow in color, with a diameter of approximately 50 / nm ~ 500 / nm and a length are up to 500 /μm.

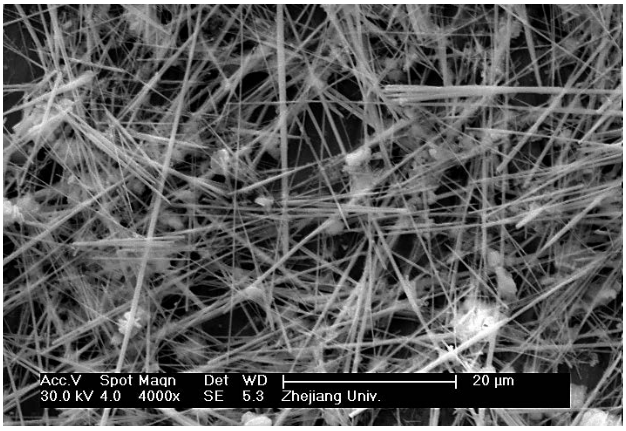

Figure 1 SEM image of $PbTiO_3$ nanowires

Preparation of EBSD specimens

The EBSD sample requires a highly smooth surface, so after the $PbTiO_3$ nanowires are made into a suspension, they are dispersed by ultrasonic waves and dropped on the sample carrier plate, and then aligned with the crystal plane of a single grain in the horizontal direction for testing.

The EBSD sample stage is at a 70,5 º angle to the direction of the electron beam. When bombarded by the electron beam in a high-power field of view, it is easy to cause the sample wriggle, which affects the experimental results. Dropping suspension on the EBSD sample stage can prevent the wriggle.

Results and discussion of EBSD experiment

A $PbTiO_3$ grain was selected on the SEM page, and the SEM image of the grain is shown in Figure 2.

During the experiment, two signal collection methods were attempted to collect electron backscatter diffraction pattern. One method is to adjust the magnification to over 200 000 and use "TV" mode for collection. Due to the high magnification of this method, the sample exhibits significant wriggle and the quality of the image is poor, as shown in Figure 3(a). Another method is to use a "spot" mode for scanning at a lower magnification. This method avoids the adverse effects of sample wriggle at high magnification, and the image is clearer, as shown in Figure 3(b).

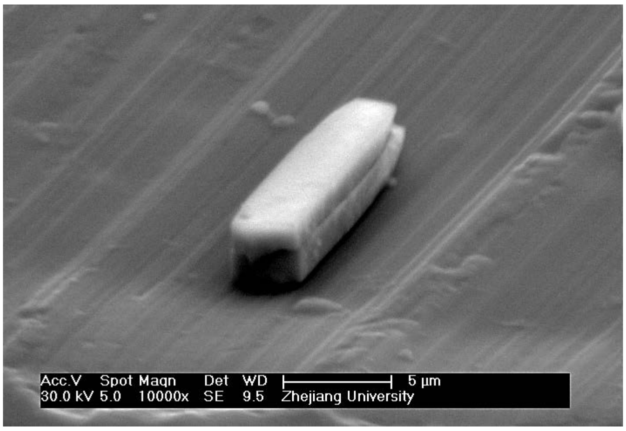

Figure 2 SEM image of $PbTiO_3$ grain crystal

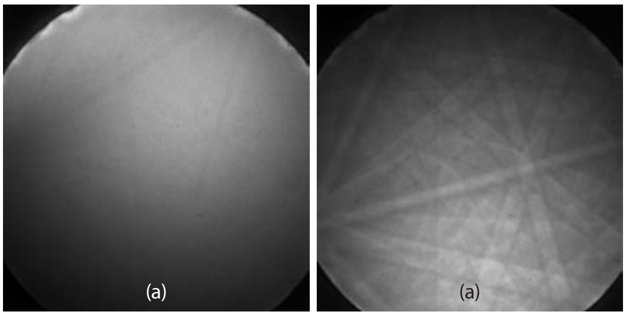

Figure 3 Electron backscatter diffraction pattern of $PbTiO_3$ nanowire: (a) Image in "TV" mode; (b) Image in "spot" mode

Loading the $PbTiO_3$ material file directly, it was found that the calibration results were basically consistent with the results shown in the material file. The image after calibrating the index is shown in Figure 4.

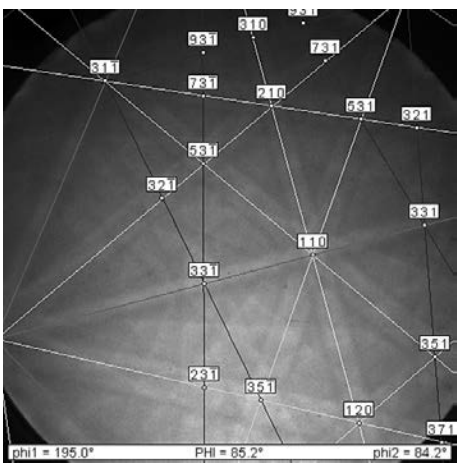

Figure 4 Electron backscatter diffraction pattern with unknown data

The crystal structure of the $PbTiO_3$ obtained in the experiment is a tetragonal structure, the P4mm (99) space group, and the cell parameter is cell = 3,905 × 4,156 Å. The crystal face growing in the direction of <110> is $(\bar{1}10)$, and belongs to the {110}crystal family.

Comparison of EBSD and XRD

$PbTiO_3$ powder was tested by X-ray diffraction (XRD), as shown in Figure 5, and the corresponding parameters were shown in Table 1.

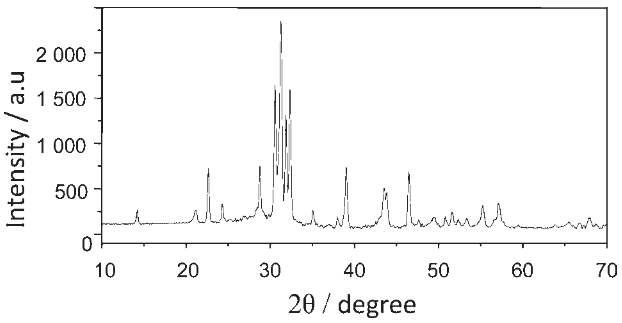

Figure 5 XRD pattern of $PbTiO_3$ nanowires

Tabale 1 **Parameters of XRD**

2θ (°)	(h k l)	2θ (°)	(h k l)	2θ (°)	(h k l)
21,362	(001)	49,656	(102)	67,824	(220)
22,753	(100)	51,682	(201)	70,361	(212)
31,408	(110)	52,345	(210)	72,016	(221)
32,396	(101)	55,281	(112)	72,311	(103)
39,135	(111)	57,166	(211)	72,564	(300)
43,516	(002)	65,549	(202)	76,648	(301)
46,471	(200)	67,563	(003)	76,937	(113)

From the Figure 5, it can be seen that the third line on the left has the highest intensity, and according to the table, it corresponds to 2θ = 31,408°, with a diffraction surface of (110) crystal plane, consistent with the EBSD test results. The crystal structure of $PbTiO_3$ detected by XRD is P4mm (99), and the cell parameter is cell = 3,905 × 4,156 Å, which is consistent with the EBSD results that $PbTiO_3$ has a tetragonal structure.

CONCLUSIONS

By hydro-thermal method, the $PbTiO_3$ nanowires have been successfully made with the chemical grade tetrabutyl titanate ($(C_4H_9O)_4Ti$) and lead nitrate $Pb(NO_3)_2$ as starting materials, potassium hydroxide as the mineralizer, polyvinyl alcohol (PVA) and PAA, PEG as additives.

The crystal structure of $PbTiO_3$ is P4mm (99), and the cell parameter is cell = 3,905 × 4,156 Å.

$PbTiO_3$ nanowires is investigated by EBSD, and XRD. The experimental results of EBSD are accordant with that of XRD, which illuminates that surface EBSD analysis technique is feasible to determine crystal structure and orientation of powder material with new structure.

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Note: The responsible translator for English is Yan Wu, University of Science and Technology Liaoning, Anshan, China