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PREPARE METHOD OF THE NEW STRUCTURE $PbTiO_3$ NANOWIRES

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When the self-made with Teflon lined with stainless steel reaction kettle is used to produce $PbTiO_3$ nanowires with the adoption of hydrothermal reaction .The crystal structure of nanowire was analyzed by X-ray diffraction (XRD) and electron backscatter diffraction (EBSD). The results indicate, $PbTiO_3$ nanowires with new structure can be made when Pb / Ti equals 2,2.

Key words: $PbTiO_3$, nanowires, new structure, X-ray researeh (XRD,EBSD,SEM)

INTRODUCTION

Recently, ferroelectrics oxide nanostructures including nanorod, nanowire and nanodisk are of great interest not only for their theory richness in nanoscale ferroelectricity and piezoelectricity, but also because of their great potential applications in super high density data storage and nanometer-scale electromechanical systems (NEMS) [1-3].

$PbTiO_3$ (PT) is an important ferroelectrics with a high Curie Point Tc 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 [4-6]. However, it is difficult to obtain the dense ceramic of pure $PbTiO_3$ when undergoing the phase transition from cubic to tetragonal phase with large strain 6,4 %, breaking the ceramic. In most cases, $PbTiO_3$ is used in the formation of thin film or as an end member for piezoelectric ceramic systems [7-8]. With the miniaturization of piezoelectronic and electromechanical devices, the requirements for free standing nanostructures that can be applied to these devices keep increasing [9].

The hydro-thermal reaction is used to make $PbTiO_3$ nanowires, whose crystal structure is analysed with the adoption of Electron Backscattered Diffraction (EBSD) and X-ray Diffraction (XRD) in this study. The results indicate , $PbTiO_3$ nanowires with new structure can be made when Pb / Ti equals 2,2.

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EXPERIMENT

Major reagents

Chemical grade tetrabutyl titanate ($(C_4H_9O)_4Ti$) and lead nitrate $Pb(NO_3)_2$ were used as starting materials, potassium hydroxide as the mineralizer, polyvinyl alcohol (PVA) and PAA, PEG as additives, all of which are analytically pure reagents bought in the market.

Preparation methods

The hydro-thermal reaction of for prepared $PbTiO_3$ 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 prepared the precipitated TOH, ammonia was used as precipitant. $(C_4H_9O)_4Ti$ was dissolved in deionized ethanol to form 0,1 / M Ti^{4+} solution. Subsequently, the precipitated TOH was prepared by introducing the Ti^{4+} solution into a 0,15 / M ammonia 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 0,1 / M, a KOH concentration of 2 / M 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.

Two samples have been made for this study. Sample 1 in this work was prepared with Pb / Ti = 1 and 24 h reaction processing. For obtaining sample 2, Pb / Ti = 2,2 was used as key condition under hydrothermal processing with reaction time of 8 h. The products were filtered and washed several times with distilled water and absolute ethanol, and finally oven dried in air at 60 °C for 24 h, resulting in the formation of gentle yellow powders for two samples.

RESULTS AND DISCUSSIONS

Figure 1(a) is the scanned picture taken through the electron microscope, whose diameters range from about 40 / nm to 500 / nm , and whose lengths are up to 400 / µm. The scanning electron microscopy (SEM) image indicates, accompanying with large-scale wires, there is still partial particles existing.

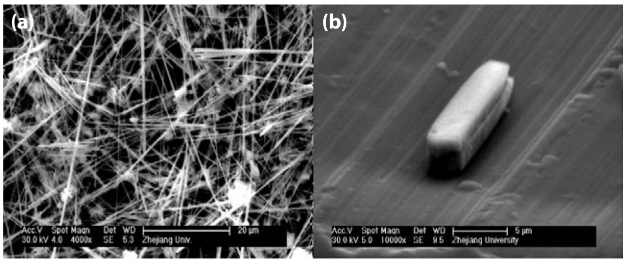

Figure 1 SEM image of $PbTiO_3$ nanowire.

The backscattered electron diffraction analysis has been made on the even surface of the linear crystal so far as Figure 1(b) is concerned. The kikuchi pattern measured is seen in Figure 2(a); while the kikuchi pattern calibrated is shown in Figure 2(b). 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 x 4,156 Å. The crystal face growing in the direction of <110> is (110), and belongs to the {110} crystal family. Analysis and test of EBSD have been made to different nanowirse in order to verify the validit of the result. During the process of the repetitive structure test of the nanowires, a kind new crystal structure of $PbTiO_3$ nanowire's, which can not be analysed by means of the current database of the EBSD as shown in Figure 2(c).

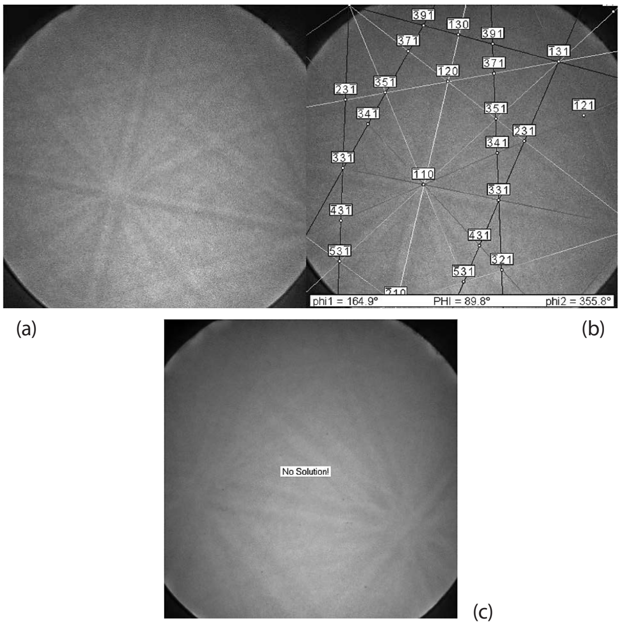

Figure 2 Kikuchi pattern of $PbTiO_3$ nanowire. (a) Kikuchi pattern obtained from the collection of the crystal grains as seen in Figure 1(b). (b) Kikuchi pattern calibrated in Figure (a). (c) Kikuchi pattern with unknown data.

Such being the case, XRD has been made to Sample 1, and the new structure has been verified to be existing as shown in Figure 3. A new set of diffraction peaks occurred, which can be indexed on a tetragonal unit cell with a = 12,35 / Å, c = 3,83 / Å. By careful analysis, this structure belongs to I422 (97) space group. The structure obtained by XRD here does not agree with any other known structures concerning with $PbTiO_3$ [10, 11].

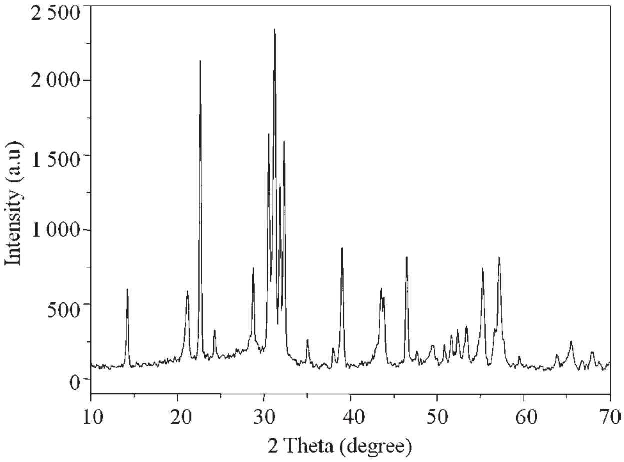

Figure 3 XRD pattern of sample 1 of $PbTiO_3$ nanowire.

The XRD analysis of Sample 2 as shown in Figure 4(a) shows that the structures of the nanowires produced with Pb / Ti = 2,2 are all of the new one.

For further detecting the new structure existing in this sample, a first-principles simulation method was conducted to get the XRD pattern with a = 12,35 / Å, c = 3,83 / Å unit cell for $PbTiO_3$ [12]. By this method, a large unit cell of $PbTiO_3$ was obtained with 40 atoms and Pb:Ti:O =1:1:3, as shown in Figure. 4(b).

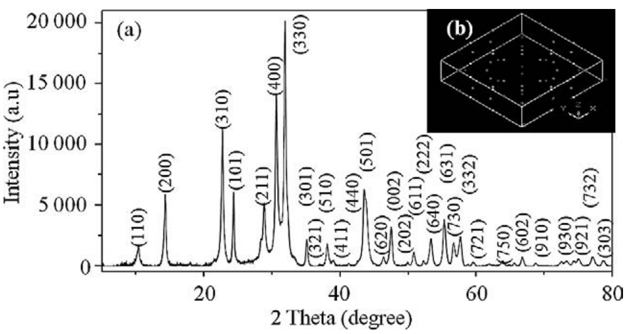

Figure 4 Characterization of $PbTiO_3$ new structure in sample 2 by XRD patterns.

(a) XRD pattern of sample 1 after indexing. (b) Simulated unit cell of $PbTiO_3$ new structure by a first-principles calculation according to XRD pattern result in (a).

CONCLUSIONS

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 when hydro-thermal method is used. The specific value of Pb / Ti influences greatly on the structure of the nanowires, and when Pb / Ti = 2,2 is used as the key condition under hydrothermal processing with reaction time of 8 h, the $PbTiO_3$ (PT) nanaowires with a new structure can be made.

The structure tests of different nanocrystals can be made repeatedly through the use of backscattered electron diffraction so as to acquire the right result. However, the EBSD technology has some certain limitations due to the fact that EBSD technology has been little used in the nanomaterials field, where the database is relative ly short.

Acknowledgements

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