When the self-made with Teflon lined with stainless steel reaction kettle is used to produce PbTiO₃ 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, PbTiO₃ nanowires with new structure can be made when Pb / Ti equals 2.2.

**Key words:** PbTiO₃, nanowires, new structure, X-ray research (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].

PbTiO₃ (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 PbTiO₃ when undergoing the phase transition from cubic to tetragonal phase with large strain 6.4 %, breaking the ceramic. In most cases, Pb-TiO₃ 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 PbTiO₃ 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, PbTiO₃ nanowires with new structure can be made when Pb / Ti equals 2.2.
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.

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 PbTiO₃ 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 nanowire in order to verify the vality of the result. During the process of the repetitive structure test of the nanowires, a kind new crystal structure of PbTiO₃, nanowire’s, which can not be analysed by means of the current database of the EBSD as shown in Figure 2(c).

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 PbTiO₃ [10, 11].

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 PbTiO₃ [12]. By this method, a large unit cell of PbTiO₃ was obtained with 40 atoms and Pb:Ti:O =1:1:3, as shown in Figure 4(b).

(a) XRD pattern of sample 1 after indexing. (b) Simulated unit cell of PbTiO₃, new structure by a first-principles calculation according to XRD pattern result in (a).
CONCLUSIONS

The PbTiO₃ nanowires have been successfully made with the chemical grade tetrabutyl titanate ((C₄H₉O)₄Ti) and lead nitrate Pb(NO₃)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 PbTiO₃ (PT) nanowires 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 relatively short.

Acknowledgements

This work was supported financially by the National High Technology Research and Development Program of China (grant no. AQ62002AA332100), the National Natural Science Foundation of China (50271065), and the 35 Zhejiang Provincial Foundation of Advanced Research Project (20041207).

References


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