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Rietveld analysis of ferroelectric $PbZr_{0.525}Ti_{0.475}O_3$ thin films

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Abstract

A procedure to obtain all the components of crystal structure by simultaneous Rietveld refinement of X-ray diffraction pattern collected is described. The specimens used were lead zircone titanate (PZT) thin films prepared by chemical solution deposition (CSD) and deposited on Si (1 0 0) and Si (1 0 0)/Pt (2 0 0) substrates. The growth condition to obtain high quality epytaxial of thin lead zircone titanate was carried out by spin coating at angular velocities 2500, 3000, 3500 rpm for 30 s and they were annealed at 750 °C for 3 h. We made single and multi layers films. For 21 specimens with different treatments, we have refined eight parameters which include lattice parameters, background, absorption coefficient, atomic positions, two theta zero error, thermal factors, and profile peak functions. Most of the samples show that the crystal structures are tetragonal with space group *P4mm*. Thermal effect and profile function refinement make were fitted better than other effect in the refinement. The plane orientations (1 0 0) and (2 0 0) sometimes were noticed as an effect of substrate, but it was confirmed indeed the growth of PZT thin film.
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Keywords: D. PZT; Rietveld analysis; Thin films

1. Introduction

The thin films of $PbTiO_3$ and $PbZr_xTi_{1-x}O_3$ (PZT) have been used as pyroelectric IR detector. Merit of pyrosensor compared to other infrared sensor materials such as semiconductors: wide range of response frequency, used at room temperature, quick response in comparison with other temperature sensors and high quality materials for pyrosensor is unnecessary. PZT films can be grown by various methods, such as sputtering, chemical solution deposition (CSD), pulse laser deposition (PLD) and metal organic chemical vapor deposition (MOCVD).

One of the PZT elements is $PbTiO_3$. $PbTiO_3$ is ferroelectric at room temperature and has a Curie temperature at 490 °C as reported first by Shirane et al. and independently by Smolenskii. Subsequent investigations of the properties of this ceramic have provided comparative data for barium titanate. The structure of $PbTiO_3$ is isomorphic with $BaTiO_3$ in which there is a tetragonal distortion from cubic perovskite lattice at room temperature. One of the deficiencies of lead titanate as compared to $BaTiO_3$ is that $PbTiO_3$ is unstable because of the loss of PbO at higher temperature. Nevertheless, lead titanate has a relatively lower melting point as compared with barium titanate. This characteristic could be used as reference for structure of PZT.

Crystal structure analysis is important step to get the high quality of PZT. The atomic structure of PZT solid solutions near the morphotropic phase boundary (MPB) was examined by using time-of-flight neutron diffraction. PDF analysis showed that Ti is always ferroelectrically active, while Zr is not. XRD method is general technique to find out micro parameter of materials, otherwise another technique is needed to refine data from XRD data [1]. This method is made for accurate data. In this paper, Rietveld analysis is used to refine structure and micro parameter of PZT material.

2. Experimental procedure

PZT thin films were fabricated by CSD methods [1–4] using 0.83 g PZT as precursor in 5 ml 2-methoxyethanol

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($H_3COCH_2CH_2OH$, 99.9%) was used as solvent and then using ultrasonic Model Branson 2210 for 1 h to get the clear liquid. After 20 min of standing at room temperature, this solution acquired a milky appearance. It contained equivalent 0.5 M PZT. After 2 h of aging, the solution described above was applied on 12 mm × 12 mm Si (1 0 0)/Pt (2 0 0) substrates and then prepared by spin coating at 2500, 3000 and 3500 rpm for 30 s. The post deposition annealing of the films was carried out in a Furnace Model Nabertherm Type 27 at 750 °C for 3 h in an air atmosphere. The structure of the films was analyzed by X-ray diffraction (XRD) [5,6].

Philips PW1877 X-ray diffractometer available at Materials Science Program, Department of Physics University of Indonesia was used to obtain room temperature diffractograms for the representative samples. The X-ray diffraction data were then refined using GSAS, which was developed by Allen C. Larson and Robert B. Von Dreele from Los Alamos National Laboratory USA, installed on a Pentium IV 2.4 GHz computer with 512 MB of RAM, either for structural parameters or electron density as well [7–9].

Nomenclature of sample depends on composition and treatment. For example: PZTSI25, it means PZT on Si (1 0 0) substrate, 0.25 M and prepared by spin coating at 2500 rpm. If more than one layer and different concentration use alphabet after substrate name, for example PZTSIA30, it means PZT on Si (1 0 0) substrate, 0.5 M and prepared by spin coating at 3000 rpm and one layer, *A* means 0.5 M and two layers, *B* means 0.5 M and three layers, *E* means 0.25 M and one layer and *P* means 0.25 M and three layers.

3. Result of the Rietveld analysis

The XRD refine results are presented in this section. We have allowed the position of Zr and Ti atoms to be refined independently, beside that we use constraint for this atoms. We design Pb position in unit cell constant. Various results were described in graph, generally PZT structure in room temperature (300 K) is tetragonal, instead of a certain condition is quasi-cubic (Figs. 1–6).

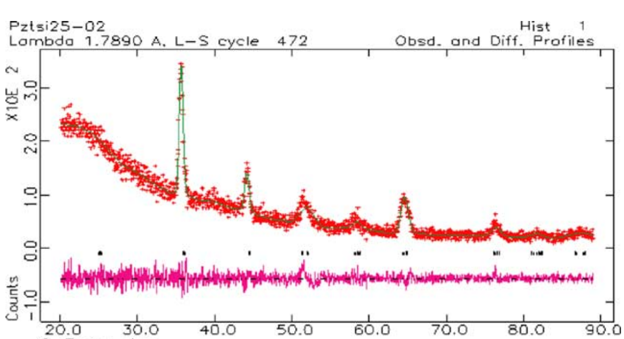

Fig. 1. PZT Si 2500 rpm: $a = b = 4.076697$, $c = 4.125827$, Rp = 8.72%, Rwp = 11.96%.

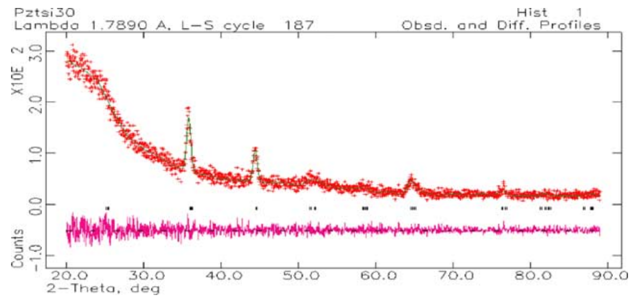

Fig. 2. PZT Si 3000 rpm: $a = b = 4.07643$, $c = 4.121686$, Rp = 9.16%, Rwp = 12.85%.

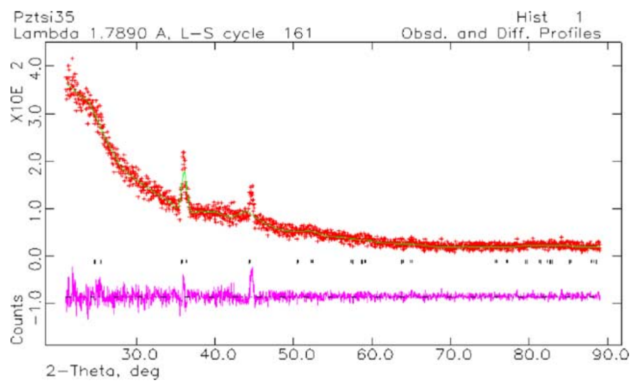

Fig. 3. PZT Si 3500 rpm: $a = b = 4.062459$, $c = 4.197224$, Rp = 8.15%, Rwp = 11.75%.

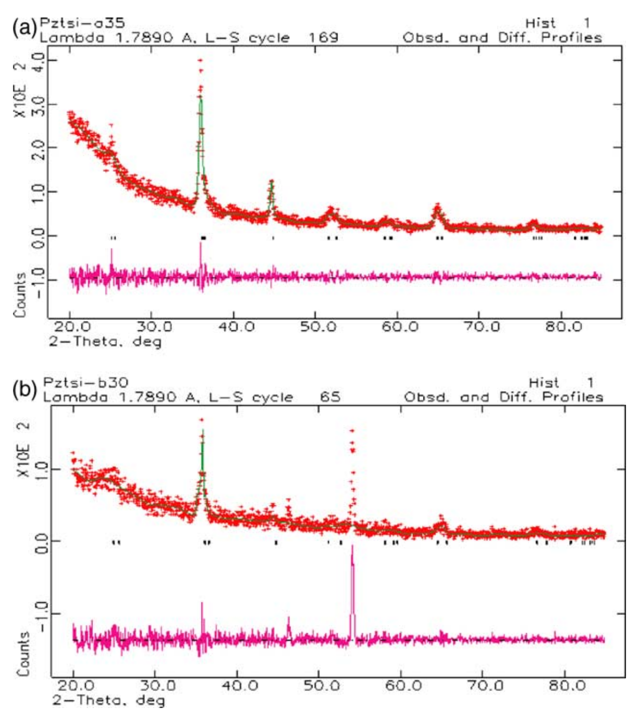

Fig. 4. (a) PZT Si A 3500 rpm: $a = b = 4.047431$, $c = 4.107386$, Rp = 9.84%, Rwp = 13.60%. (b) PZT Si B 3000 rpm: $a = b = 4.051984$, $c = 4.124606$, Rp = 16%, Rwp = 22.72%.

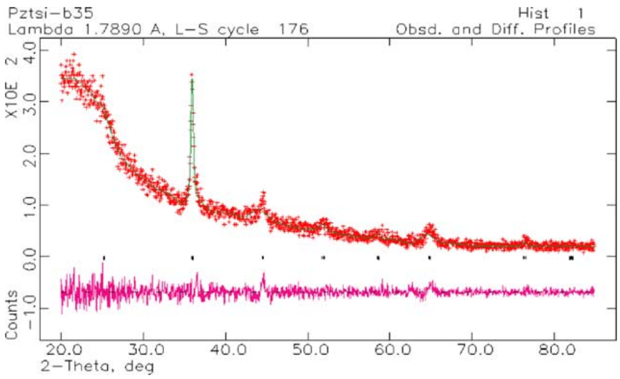

Fig. 5. PZT Si B 3000 rpm: $a = b = 4.051984$, $c = 4.124606$, Rp = 16%, Rwp = 22.72%.

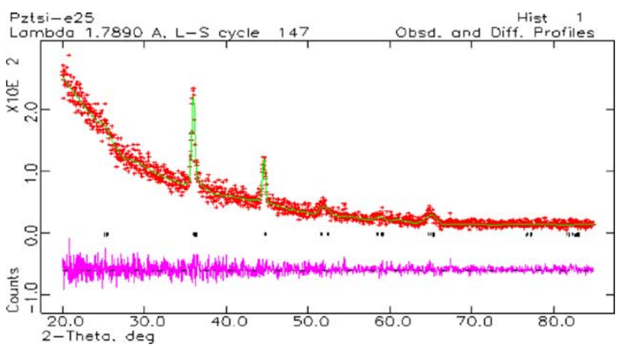

Fig. 6. PZT Si B 3500 rpm: $a = b = 4.094656$, $c = 4.084748$, Rp = 7.82%, Rwp = 11.06%.

4. Summary

We have examined the structure of 21 samples of PZT in room temperature using the Rietveld refinement. The Rietveld results described the “quasi-real” structure of PZT thin films in spite of the actual local structure being significantly different. Rietveld did constraint treatment to PZT which caused the probability of position of Ti/Zr which was not sure. This treatment was done to reduce overlap position in the same place between Ti and Zr.

For 21 specimens with different treatments, we have refined eight parameters include lattice parameters, background, absorption coefficient, atomic positions, two theta zero error, thermal factors, and profile peak functions. Most of the samples show that the crystal structure is tetragonal with space group is *P*4*mm*. Some sample especially with Si (1 0 0) substrates show some quasi-cubic structures. The thermal effect and profile function refinement make fitted better than other effect in refinement. The pseudo-Voigt description of profile shape was determined as profile set up for Rietveld refinement. Refinement profile function value use modern commercial Bragg–Brentano diffractometer and value of the sample broadening. The plane orientations (1 0 0) and (2 0 0) sometimes were noticed as an effect of substrate, but it was indeed the growth of PZT thin film which was confirmed.

Acknowledgements

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