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Crystal Structure Analysis of Ferroelectrics by Profile Analysis Method

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Profile analysis method originally devised by Rietveld for refining powder neutron diffraction data is examined in X-ray diffraction cases as well using Si and $BaTiO_3$ powders. Then the profile analysis is applied to both neutron data and X-ray data diffracted from $PbZrO_3$ fine powder, and a previously obtained antiferroelectric crystal model is considerably refined. Contradictions that have remained unsettled between the structural and the dielectric properties of $PbZrO_3$ is resolved.

§1. Introduction

Profile analysis of powder neutron diffraction data, originally developed by Rietveld[1,2] has now become an important method for the refinement of crystal structures.[3-9] Recently, powder X-ray diffraction data have also been analyzed with the same principle.[10-12]

Obviously, single crystal methods are the most important technique; however an inherent disadvantage is found in ferroelectrics that they normally contain twin structures, which often make the precise estimates of the structure factor $F_0(h, k, l)$ very difficult. By applying the advanced profile analysis method to powder diffraction data which are highly reliable, it seems possible to refine the crystal structure of ferroelectrics considerably.

In the present study, we at first demonstrate the usefulness of the profile analysis method in powder X-ray diffraction data of Si and $BaTiO_3$. Then the method is applied to both X-ray and neutron diffraction data of $PbZrO_3$. An appreciable refinement of the structure has been achieved.

§2. Analysis of Powder X-ray Diffraction Data

Samples, Si and $BaTiO_3$, are high purity powders of fine particles with dimensions of less than 5 μm. X-ray data were collected as a function of 2θ (θ: Bragg angle). The sample and the counter were scanned continuously in the $\theta - 2\theta$ mode at a speed of 0.25° (2θ)/min; and the accumulated diffraction countings were registered at every 10 sec ($\Delta 2\theta = 1/24$ degree) on recording tapes which were used later with Rietveld's program.

Least-squares refinement of structural parameters were carried out by minimizing the quantity

$$M = \sum_i w_i \left| Y_i\,(\mathrm{obs}) - \frac{1}{k} Y_i\,(\mathrm{cal}) \right|^2, \qquad (1)$$

where Y_i (obs) and Y_i (cal) are the observed and the calculated diffraction intensities at $2\theta_i$; k and w_i are the scale factor and weight, respectively. In the calculation of Y_i (cal) it is assumed that each diffraction line has approximately a modified Lorentzian shape.[12]

In the analysis of Si, computation was initiated by assuming that atoms are on general positions, split atoms model being used; and the present result is in good agreement with the widely accepted ones.[13]

The result for tetragonal $BaTiO_3$ powder is shown in Table I: structural parameters ob-

Table I. Structural paramaters for $BaTiO_3$ data. $R_{\mathrm{Bragg}} = 0.036$ and $R_{\mathrm{profile}} = 0.122$.

	Present result	Harada et al.[14]	Frazer et al.[15]	Glazer et al.[16]
ΔZ_{Ti}	0.013(4)	0.0135(4)	0.014(2)	0.016(5)
$\Delta Z_{O(1)}$	-0.028(4)	-0.024(1)	-0.0249(6)	-0.026(14)
$\Delta Z_{O(2)}$	-0.013(4)	-0.0150(4)	-0.0156(7)	-0.010(22)
B_{Ba}	0.55(1)	0.45(6)	0.36(8)	0.48(2)
B_{Ti}	0.50(4)	0.30(20)	0.50(6)	0.43(6)
$B_{O(1)}$	0.39(11)	0.49(6)	0.41(4)	0.38(46)
$B_{O(2)}$	0.39(11)	0.52(3)	0.49(4)	0.43(23)
a	3.9945(1)			
c	4.0330(2)			

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tained in this study also agree with previously published ones very well.[14-16]

Both results obtained in Si and $BaTiO_3$ powders demonstrate clearly the usefulness of the profile analysis method when applied to X-ray data.

§3. Crystal Structure of $PbZrO_3$

The space group of antiferroelectric $PbZrO_3$ originally adopted by Sawaguchi *et al.* in 1951 was D_{2h}^9-Pbam which is non-polar.[17] The crystal model was refined by Jona *et al.*,[18] reporting that $PbZrO_3$ is antiferroelectric in *a-b* plane and polar in the *c*-direction (C_{2v}^8-Pba2), which means a presence of a large spontaneous polarization P_s. However, recent investigations on the dielectric properties have made rather a denial of the presence of P_s.[19,20]

Since no good single crystal of $PbZrO_3$ without domain structure has been available, the proper strategics for obtaining reliable structural information seems an adoption of profile analysis method for both X-ray and neutron diffraction data. X-ray data were collected in almost the same manner as mentioned above. Powder neutron data were collected using powder sample as well as a ceramic rod. Each line shape of the diffracted peak has been assumed conventionally as of Gaussian.[2]

The guidline of the analysis was: 1) use the X-ray data principally to refine parameters of heavy atoms (Pb and Zr), 2) for the de-

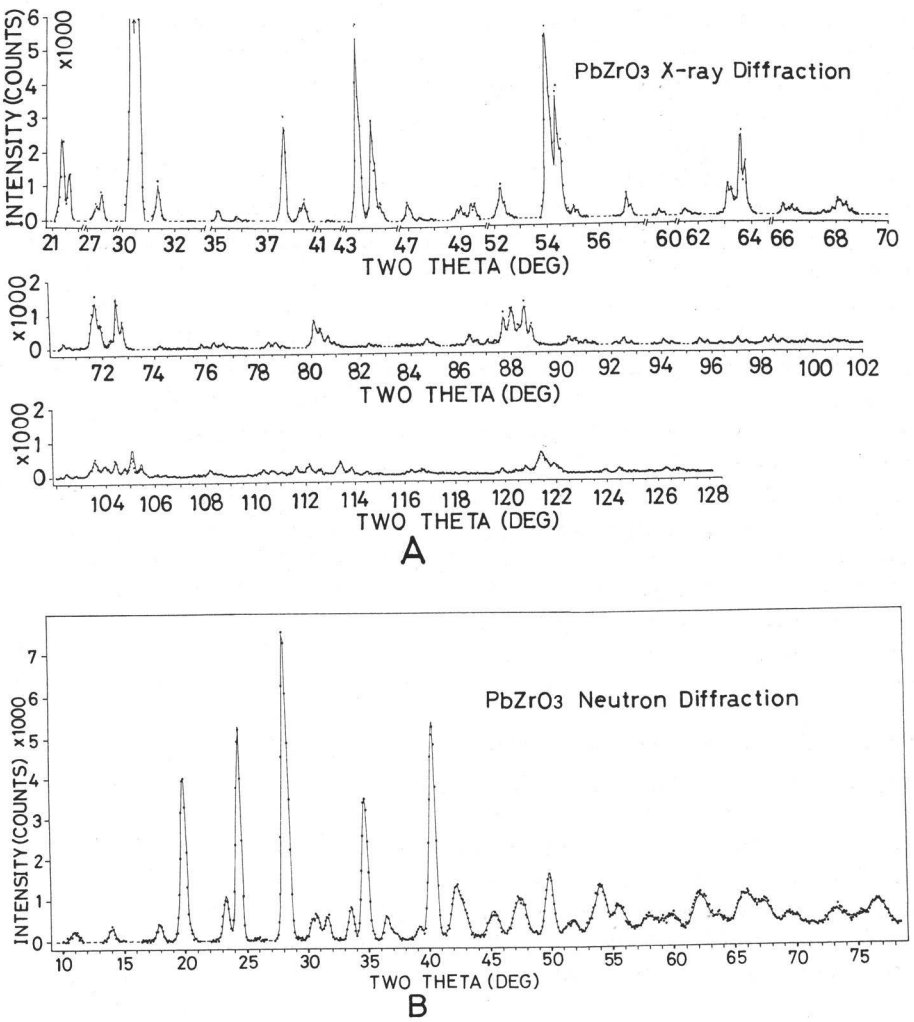

Fig. 1. The observed and the calculated powder diffraction profiles of $PbZrO_3$. A) X-ray diffraction using Cu-Kα. B) Neutron diffraction at $\lambda = 1.007$ Å.

termination of oxygen parameters, make an exclusive use of the neutron data, 3) repeat the both processes 1) and 2) alternatively until each minimum of M's, given in eq. (1) for both X-ray and neutron cases, is obtained.

We examined both space groups of C_{2v}^8 and D_{2h}^9 and found that the least-squares refinements led to almost the same structural parameters, therefore D_{2h}^9 is the reasonable choice. Present result is shown in Table II; and the observed and calculated diffraction profiles are shown in Fig. 1. It turns out that interatomic distances are also reasonable and the crystal is non-polar; schematic view of the structure is shown in Fig. 2. Details of the analysis will be published elsewhere.

Table II. Fractional coordinates of atoms in $PbZrO_3$ at room temperature. Weighted reliability factors for the X-ray and neutron cases are: $R_{wp}(X)=0.135$ and $R_{wp}(N)=0.075$.

	x	y	z	B (Å^2)
Pb	0.7064(2)	0.1247(3)	0.0	1.01(2)
Pb'	0.7064(2)	0.1285(3)	0.5	1.01(2)
Zr	0.2423(3)	0.125(1)	0.2416(5)	0.06(3)
O1	0.269(2)	0.155(2)	0.0	0.59(3)
O1'	0.291(3)	0.096(2)	0.5	0.59(3)
O2	0.032(2)	0.2610(6)	0.283(1)	0.59(3)
O3	0.0	0.5	0.206(2)	0.59(3)
O4	0.0	0.0	0.248(2)	0.59(3)

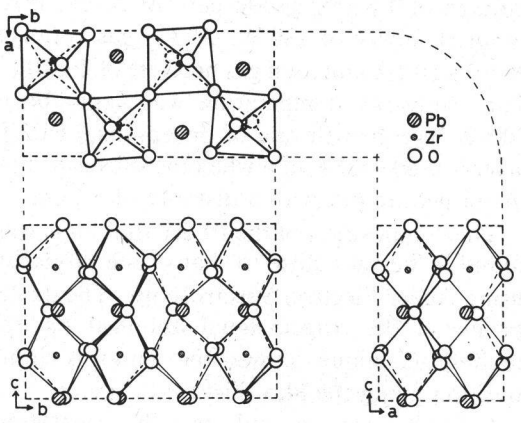

Fig. 2. Schematic view of ZrO_6 octahedra network of $PbZrO_3$, projected along *c*, *a* and *b*.

§4. Conclusions

The present study has confirmed the usefulness of profile analysis methods when applied to powder X-ray diffraction data of ferroelectrics. Antiferroelectric structure of $PbZrO_3$ has also been refined considerably; no spontaneous polarization exists, and repugnances between the crystal structural properties and the dielectric properties have clearly been resolved.

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