論文の内容の要旨

論文題目 : An application of the MaxEnt/fragment EP method to ferroelectric polarization analysis (マキシマムエントロピー法による静電ポテンシャルフラグメント解析法の強誘電分極解析への応用)

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1. Introduction

Designing and controlling of intense local polarization in solids are vital for emerging electronics, such as high-performance field-effect transistors, FeRAMs and multiferroic devices in nano-scale[1]. Neither microscopic characterization nor design of individual dipoles, however, has been intensively investigated so far: the properties have been mainly described in terms of macroscopic properties based on measurements of electric polarization *P* under electric field *E* for bulk samples. Recently, the electrostatic potential (EP) analysis based on electron charge density using maximum entropy method (MEM) has been developed for the characterization of specific features originating from the electrostatic field/force in microscopic scale[2~4]. Using the MEM/EP analysis, we have succeeded in visualization of relation between internal electric field and physical properties, such as thermal conductivity affected by rattling[5] and superconductivity related to the bipolaron[6]. In this research, we investigated the polarization of ferroelectric materials, $PbTiO_3$, $BaTiO_3$ and Bi_2SiO_5, within a fragment unit based on the electron charge density combined with electrostatic potential analysis.

2. Procedure of MaxEnt/fragment EP method for the determination of local and total polarization

Flowchart of the MaxEnt/fragment EP method is shown in Figure 1. Synchrotron X-ray powder diffraction measurement was carried out at BL02B2 in the SPring-8. The measurement wavelength was 0.40058(1) Å and 0.35206(1) Å for Perovskite materials ($PbTiO_3$ and $BaTiO_3$) and Bi_2SiO_5, respectively. Obtained data were analyzed by the MEM/Rietveld method. For the estimation of accurate polarization values, electron charge density obtained by the final cycle of MEM analysis was used as negative charge, while atom positions by Rietveld analysis were used as nuclear (positive charge) positions. For the determination of a fragment, the trace of local minimum of EP with a pair of cation and anion was defined as the boundary of the fragment: the spatial variation of EP $U(r)$ is obtained by the sum of electron- and nucleus-charge components, $U_{ele}(r)$ and $U_{nuc}(r)$, respectively[4]. The polarization based on the MaxEnt/fragment EP method is obtained by the equation (1).

$$\vec{P} = \frac{e}{V}\left[\sum_i A_i\{(X_i - x_o)\hat{x} + (Y_i - y_o)\hat{y} + (Z_i - z_o)\hat{z}\} - \{\int (x_i - x_o)\rho_i(x_i)dx_i\hat{x} + \int (y_i - y_o)\rho_i(y_i)dy_i\hat{y} + \int (z_i - z_o)\rho_i(z_i)dz_i\hat{z}\}\right] \quad (1)$$

,where e and V is elementary charge (1.602×10^{-19} C) and the unit cell volume, respectively. A_i and (X_i, Y_i, Z_i) are atom number and position of ith atom. (x_o, y_o, z_o) are position of the center of mass in the fragment unit. $\rho_i(x_i, y_i, z_i)$ is the electron density located at ith pixel. (x_i, y_i, z_i) are the position of ith pixel for electron charge contribution. $(\hat{x}, \hat{y}, \hat{z})$ are the unit vectors, and integration is carried out over the fragment unit.

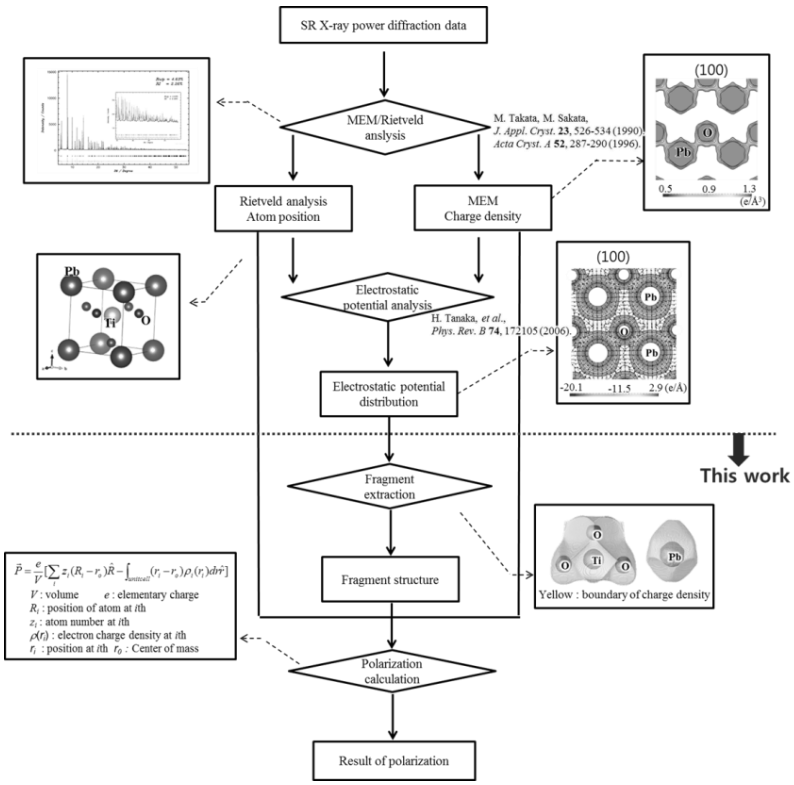

Figure 1. Procedure of analysis for the determination of local/total polarization values by MaxEnt/fragment EP method.

3. Result and Discussion

3.1. Reference application to the typical ferroelectrics: Perovskite structure $PbTiO_3$ and $BaTiO_3$

$BaTiO_3$ and $PbTiO_3$ are well-known as typical ferroelectric materials with Perovskite structure. To verify a validity of our method, polarization values of $PbTiO_3$ and $BaTiO_3$ were estimated by MaxEnt/fragment EP method. And the obtained values were compared to the reported results. The fragments in $BaTiO_3$ and $PbTiO_3$ were designated based on the following criteria: the cation was located on the center; the boundary of fragment was traced by a local minimum point between anion and the nearest neighbor cation. In those system, TiO_3 and Pb(Ba) fragments were selected; the polarization values inside fragment are listed in Table 1. At a first glance, the total polarization for $PbTiO_3$ is apparently larger than that of $BaTiO_3$ as expected. In addition, the value of $BaTiO_3$ shows a very good accordance with the value measured by PE hysteresis measurement. On the other hands, the value of $PbTiO_3$ is slightly smaller than that of *PE* hysteresis experiment. The strong Pb-O covalent character[7,8] may cause the discrepancy and needs further discussion. However, our method is found to be valid for relative order estimation of polarization of ferroelectric system.

Unit : $\mu C/cm^2$

		$PbTiO_3$	$BaTiO_3$
MaxEnt/fragment EP method	**TiO_3**	**32.9(1)**	**16.8(1)**
	Pb(Ba)	**1.6(2)**	**0.2(1)**
	Total	**33.5(2)**	**17.0(1)**
PE hysteresis		52~75	15~25
First-principle calculation		70~87	23~29

Table 1. Obtained ferroelectric polarization values of $PbTiO_3$ and $BaTiO_3$.

3.2. Application to the novel ferroelectric material Bi_2SiO_5

MaxEnt/fragment EP method was applied to the layered structure Bi_2SiO_5 (BSO). BSO has attracted much attention as alternatives to the traditional lead-based ferroelectric materials. By a structural analysis, it was found that BSO has a structural distortion induced by the phase transition from the orthorhombic (Cmcm) to the monoclinic structure (Cc) with cooling at around 673 K. It has a layered structure composed of the SiO_3 and the Bi_2O_2 layer, which were stacked each other along the a-axis.

Relatively large spontaneous polarization P_c of 14.5 μC/cm^2 along the SiO_3 chain in the $[SiO_3]^{2-}$ layer (c-axis) was predicted by the first principles calculation, while those along *a*- and *b*-axes, P_a and P_b, were estimated to be small values of 0.1 μC/cm^2 and 0 μC/cm^2, respectively[9]. From experimental *PE* measurements, however, only the P_a value of 0.8 μC/cm^2 was deduced, because the BSO crystals have thin-plate shape and electrode for *P-E* measurements can be formed on only large area of the *b-c* plane.[9] In addition, the polarization of the BSO was suggested to originate not from the Bi_2O_2 layer but from the SiO_3 layer, although most conventional ferroelectricity originates from heavy elements, such as Pb and Bi. Clarification of origin and mechanism of ferroelectricity in BSO is, therefore, crucial for further development of lead free ferroelectric materials.

In order to investigate the change of charge density caused by the phase transition, the MEM charge electron density was obtained using the integral intensity of diffraction patterns (Figure 2). At ferroelectric phase (300 K), the Bi atoms form a stronger covalent bond with one of the four-equivalent first-neighbored O atoms in the paraelectric phase (773 K). The Bi(b)-O(b) and Bi(a)-O(c) pairs form electric dipole moments, and the two neighboring electric dipoles form almost antiparallel configuration in the Bi_2O_2 layer (Figure 2(a)). On the other hand, the Si atoms in the ferroelectric phase form a stronger covalent bond (Figure 2(b)) with three of the four-equivalent first-neighbored O atoms in the paraelectric phase, giving rise to the formation of the SiO_3 fragment in the SiO_3 layer. The electric polarization of the SiO_3 fragment aligns in the ferroelectric configuration. From the MEM electron charge density analysis, the results visualized the antiferroelectric order in the Bi_2O_2 layer and the ferroelectric order in the SiO_3 layer in the ferroelectric phase. This is the reason why the large dipole moment of BSO originates from the light element of Si instead of the heavy element of Bi.

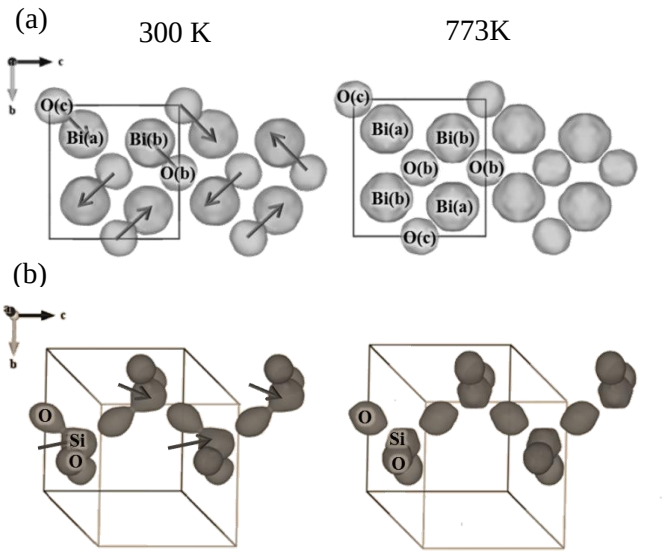

Figure 2. Dipole moment of Bi-O and SiO_3 fragment. (a) Shape of BiO_4 pyramid with the 0.85 e/Å^3 isosurface. (b) Shape of SiO_3 tetrahedral fragment with the 1.5 e/Å^3 isosurface. Arrows in (a) and (b) show the electric dipole moment expected from the structural distortion.

With MaxEnt/fragment EP method, the polarization of Bi_2SiO_5 is estimated (Table 2). The SiO_3 layer showed a large polarization along the *c*-axis (27.3(1) μC/cm^2). It should be noted that the P_b had zero due to the high symmetry of crystal structure. On the other hand, the B_2O_2 layer had small but a distinct polarization value. Total P_a and P_c of BSO were estimated to be 0.3(2) μC/cm^2 and 23.5(1) μC/cm^2, respectively. The value of P_a was roughly consistent with that predicted by the theoretical calculation (0.1

μC/cm^2) and that determined by *PE* measurements (0.8 μC/cm^2). In addition, the large P_c, value predicted by the theoretical calculation (14.5 μC/cm^2) was experimentally demonstrated by microscopic approach using MEM/fragment EP method at the first time with the value of 23.5(1) μC/cm^2. The result showed that the MaxEnt/fragment EP method using the precise X-ray diffraction data can determine the local polarization in the crystal as well as the bulk polarization values with the small amount of powder samples.

Unit : μC/cm^2

		$\|P\|$	P_a	P_b	P_c
MaxEnt/fragment EP method	**Bi_2O_2**	**4.2(1)**	**-1.8(1)**	**0**	**-3.8(1)**
	SiO_3	**27.3(1)**	**1.4(1)**	**0**	**27.3(1)**
	Bi_2SiO_5	**23.5(1)**	**0.3(2)**	**0**	**23.5(1)**
PE hysteresis	Bi_2SiO_5	-	0.8	-	-
First-principle calculation	Bi_2SiO_5	14.5	0.1	0	14.5

Table 2. The polarization of BSO in the layer and a unit cell by MaxEnt/fragment EP analysis.

4. Conclusion

We have demonstrated that the MaxEnt/fragment EP method is promising and powerful method for the ferroelectric polarization. This method opens a route for characterization and design of newly synthesized dielectric materials, and for the development of emerging dielectric materials.

References

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