Review Article

Ferroelectric Instability and Dimensionality in Bi-Layered Perovskites and Thin Films

Akira Onodera, Masanori Fukunaga, and Masaki Takesada

Department of Physics, Hokkaido University, Sapporo 060-0810, Japan

Correspondence should be addressed to Akira Onodera, onodera@phys.sci.hokudai.ac.jp

The dielectric and thermal properties of Bi (bismuth)-layered perovskite $SrBi_2Ta_2O_9$ (SBT) are discussed in comparison with ferroelectric thin $BaTiO_3$ films. Although these two perovskites exhibit quite a different nature, the dielectric properties of $BaTiO_3$ thin film are similar to those in bulk SBT. The dielectric properties and pseudo-two-dimensional structure between SBT and thin film suggest that the bulk layered ferroelectric SBT is a good model of ultra-thin ferroelectric film with two perovskite layers, free from any misfit lattice strain with substrate and surface charge at the interface with electrodes. Based on the mechanism of ferroelectric phase transition of SBT, it seems plausible that the ferroelectric interaction is still prominent but shows a crossover from ferroelectric to antiferroelectric interaction in perovskite ultra-thin films along the tetragonal axis.

1. Introduction

Barium titanate ($BaTiO_3$) is a well-known ferroelectric with perovskite structure, which has been considered to be a prototype for many oxide ferroelectrics. The dielectric constant (ε) follows a well-known Curie-Weiss law, $\varepsilon = C/(T - T_c)$, and shows a large dielectric anomaly at T_c (409 K), which has been explained by the concept of soft mode by Cochran [1, 2]. Recently, however, it has been recognized that the dielectric constant begins to decrease with decreasing the sample thickness, and shows broad and non-Curie-Weiss behavior. This evidence indicates that the well-established soft mode may be modified in the treatment of lattice dynamics of thin films of $BaTiO_3$, if the LST (Lyddane-Sachs-Teller) relation

$$\frac{\varepsilon}{\varepsilon_\infty} = \prod_j \left(\frac{\omega_{Lj}^2}{\omega_{Tj}^2} \right), \tag{1}$$

holds even in thin films as well as in bulk crystals. Furthermore, the anomalous part of specific heat (ΔC_p) changes to a very broad and unclear one in thin $BaTiO_3$ films, while it is sharp and large at T_c in bulk crystals. This suggests that the temperature dependence of an order parameter η_s (the spontaneous polarization P_s in the case of ordinary ferroelectrics) plays somewhat in different manners as the usual mean-field behavior known in typical ferroelectrics, because η_s is related to ΔC_p in the mean field theory as

$$\eta_s^2(T) = \frac{C}{2\pi} \int_T^\infty \frac{\Delta C_p}{T} dT. \tag{2}$$

As pointed out by many researches, these novel ferroelectric properties are considered to be essentially due to the two-dimensionality in thin films.

On the other hand, the similar novel dielectric behavior has been found in layered perovskite compounds. $SrBi_2Ta_2O_9$ (SBT) has been extensively studied as a candidate for ferroelectric nonvolatile memory devices [3–5]. SBT has a pseudo-two-dimensional crystal structure with two TaO_6 perovskite groups sandwiched by Bi_2O_2 semiconducting layers along the pseudotetragonal c axis within the unit cell. SBT undergoes a ferroelectric phase transition at 608 K, while the dielectric anomaly and anomalous specific heat are small in comparison with $BaTiO_3$. This similarity of crystal structures and dielectric properties between $BaTiO_3$ thin films and layered perovskite SBT shows that both materials have a common mechanism resulted in dielectric nature as discussed in the following section. Moreover, it suggests that SBT may be a good model for an ideal ferroelectric ultra-thin
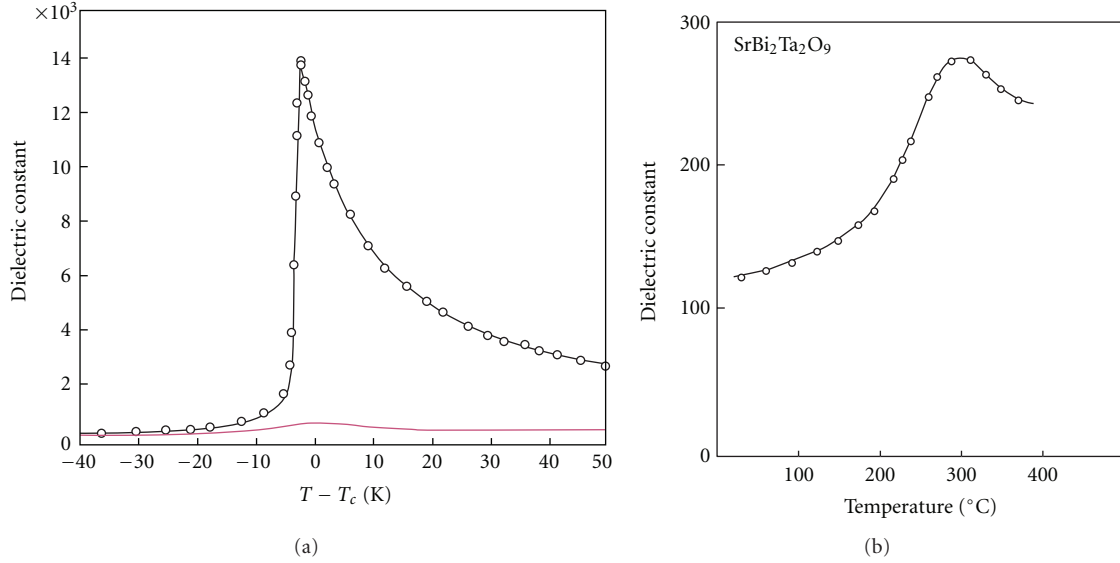
(a)

(b)

FIGURE 1: Temperature dependence of dielectric constant of (a) BaTiO$_3$ (black line) and SrBi$_2$Ta$_2$O$_9$ (red line) and (b) that of an expanded figure in SrBi$_2$Ta$_2$O$_9$ [6].

film with two perovskite unit cells, though SBT itself is a bulk crystal. In this paper, we will discuss the ferroelectric nature and stability in ultra-thin films on the basis of ferroelectric properties of Bi-layered perovskites.

2. Dielectric and Thermal Properties in BaTiO$_3$ and SrBi$_2$Ta$_2$O$_9$

The temperature dependence of ε of BaTiO$_3$ and SBT is compared in Figure 1 as a function of $(T - T_c)$ for simplicity, where T_c is a ferroelectric phase transition temperature of each perovskite, SBT, and BaTiO$_3$. The large Curie-Weiss dielectric anomaly associated with ferroelectric phase transition was noticed in BaTiO$_3$ at T_c, while a broad non-Curie-Weiss behavior was observed in layered perovskite SBT [6, 8–14]. The half temperature widths of dielectric anomalies are 10 K for BaTiO$_3$ and about 400 K for SBT, respectively. The spontaneous polarization (P_s) of SBT is relatively large (5.8 $\sim$ 10 μC/cm^2 along the a axis at room temperature), while $P_s = 26 \mu$C/cm^2 in BaTiO$_3$ along the tetragonal c axis. As P_s in SBT is the same order as those in order-disorder ferroelectrics, we expect that ε obeys the Curie-Weiss law and the peak value of ε is the order of several thousands. However, we could only observe a round peak of about 300 and weak temperature dependency around 608 K (T_c) in SBT. It is interesting to point out that similar diffuse and round dielectric anomalies were observed in ferroelectric thin films. In BaTiO$_3$ epitaxial thin films, diffuse dielectric anomaly was reported by Yoneda et al. [7, 15–18]. Thin films of BaTiO$_3$ showed a small and broad dielectric anomaly as shown in Figure 2. The peak value of ε is 1400 for 4000 Å thick film, and only 370 for 1000 Å thick film. This similarity of dielectric properties suggests the existence of some common mechanism between SBT bulk crystal and
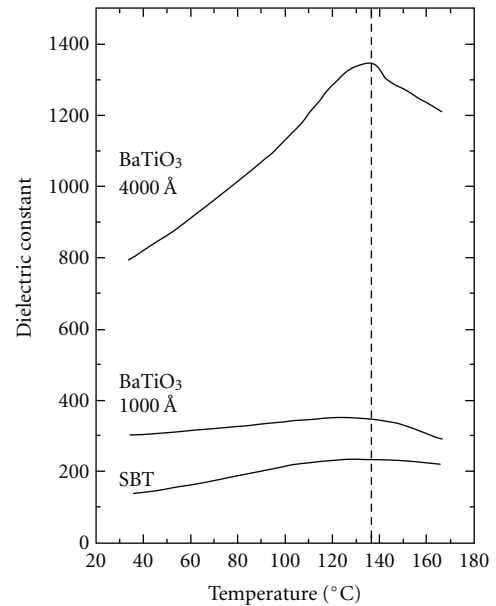

FIGURE 2: Temperature dependence of dielectric constant of SBT and BaTiO$_3$ epitaxial thin films on SrTiO$_3$ with 4000 Å and 1000 Å [7].

BaTiO$_3$ thin film. Recently, Tagantsev et al. discussed a two-dimensional strain effect on dielectric constant in perovskite ferroelectric thin films and reported a diffuse dielectric anomaly [19].

Thermal anomaly associated with the phase transition is also diffuse and widely spread in SBT as shown in Figure 3 [8, 10], while a sharp and large anomaly was found at T_c in bulk BaTiO$_3$ (Figure 4) [20]. However, the specific heat of BaTiO$_3$ epitaxial films shows diffuse temperature
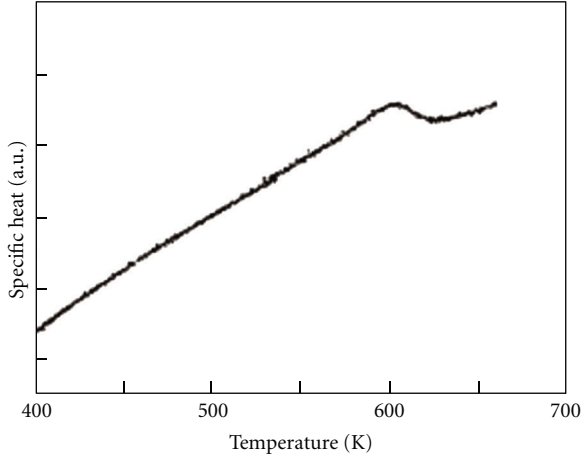
Figure 3: Temperature dependence of specific heat of $SrBi_2Ta_2O_9$ single crystal [8].
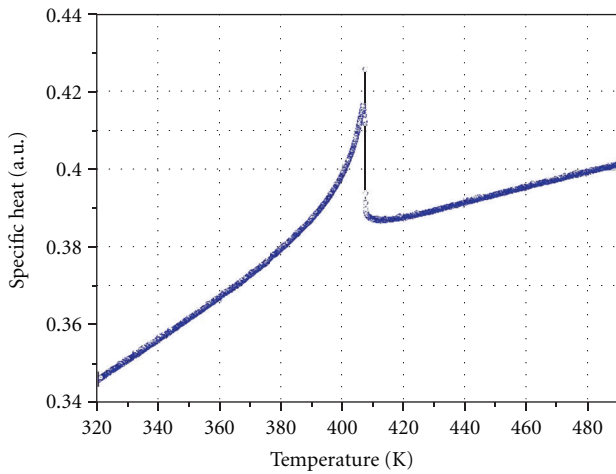

Figure 4: Temperature dependence of specific heat of $BaTiO_3$ single crystal around the paraelectric-ferroelectric phase transition point T_c [20].

dependence (Figure 5) just as those in SBT [21]. With decreasing thickness of epitaxial films of $BaTiO_3$, the shape of anomalous part of specific heat becomes round and diffuse and exhibits thermal hysteresis in those with 2000 Å and 60 Å. In $BaTiO_3$ polycrystalline thin films, a rather sharp anomaly was reported [22, 23]. The diffuse dielectric and thermal behavior observed around T_c may be attributed to the two-dimensional effect in SBT and $BaTiO_3$ epitaxial thin films.

3. Structural Analogy: Pseudo-Two-Dimensionality

$BaTiO_3$ has a prototype cubic crystal structure of perovskite in the paraelectric high-temperature phase (space group Pm3 m, with lattice parameter $a = 3.996$ Å at 393 K). It changes to tetragonal (space group P4 mm, $a = 3.992$, $c = 4.036$ Å at r. t.) associated with the paraelectric-ferroelectric

phase transition. The unit cell contains one TiO_6 octahedron at the center and Ba ions locate at the corners. The TiO_6 octahedron is tightly bonded with each other and generally considered as a hard unit, which has a regular octahedral form in the paraelectric phase. According to Slater, the correlation along the -O-Ti-O-Ti-O- chain is very strong along the tetragonal c axis and the small octahedral distortion results in ferroelectricity below T_c [26]. Epitaxial $BaTiO_3$ films were grown by on $SrTiO_3$ and MgO substrates using the activated reaction evaporation method, which were characterized by X-ray diffraction as shown in Figure 6 [24, 27]. Only the (0 0 l) reflections were observed. The submaximum peaks of the Laue function were observed around the fundamental peaks of the (0 0 1), (0 0 2), (0 0 3), and (0 0 4). The strong peaks denoted as "Sub" in Figure 6 mean the (0 0 l) reflections from the $SrTiO_3$ substrate. This evidence indicates that this film is an epitaxial crystal with a perovskite structure. Two films with thickness of 2000 Å and 60 Å were used for the specific heat measurements. The heat capacity was measured using an a. c. calorimeter.

$SrBi_2Ta_2O_9$ is a Bi-layered perovskite oxide with a highly anisotropic structure, where perovskite-type $[SrTa_2O_7]^{2-}$ groups and semiconducting $[Bi_2O_2]^{2+}$ layers are stacked alternately along the pseudo-tetragonal c axis as shown in Figure 7. The general chemical formula of Bi-layered perovskite oxides with stacking number (m) of octahedral BO_6 perovskite groups is given as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where $A = Na^+$, K^+, Ba^{2+}, Ca^{2+}, Pb^{2+}, Sr^{2+}, Bi^{3+}, $B = Fe^{3+}$, Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, and $m = 1$ to 6. Many of these compounds are ferroelectric with high transition temperatures. Ferroelectricity in SBT with $m = 2$ was discovered below 608 K (T_c) by Smolenskii et al. in 1961 [6]. The crystal structure of SBT is orthorhombic at r. t. with space group A2$_1$am ($a = 5.531$, $b = 5.534$, $c = 25.984$ Å). The lattice is highly anisotropic and pseudo-two-dimensional, and the -O-Ta-O-Ta-O- linkage along the pseudo-tetragonal c axis is interrupted by the existence of semiconducting Bi_2O_2 layers in SBT [11, 14, 25]. SBT undergoes two successive phase transitions at 608 K and 850 K. The high-temperature paraelectric phase is tetragonal with space group I4/mmm, $a = 3.927$, and $c = 25.142$ Å at 1000 K, where the TaO_6 octahedra take antiparallel arrangements along the tetragonal c axis. The crystal structures of the ferroelectric (300 K) and paraelectric phases (1000 K) were determined by X-ray diffraction as summarized in Tables 1 and 2. X-ray diffraction profile was given in Figure 8 [25].

The shape of TaO_6 octahedron is not perfect and is still distorted even in the paraelectric phase along the c axis. The Ta-O bond length owned commonly by adjacent octahedra normal to the pseudo-tetragonal c axis is a little bit short and that of O directed to Bi_2O_2 layer is long. In the ferroelectric phase, this crystal favors canted octahedral arrangements below T_c, which results in the net spontaneous polarization along the a-axis.

4. Ferroelectricity

Ferroelectricity in Bi-layered perovskite $SrBi_2Ta_2O_9$ (SBT) does not appear along the pseudo-tetragonal c axis but along
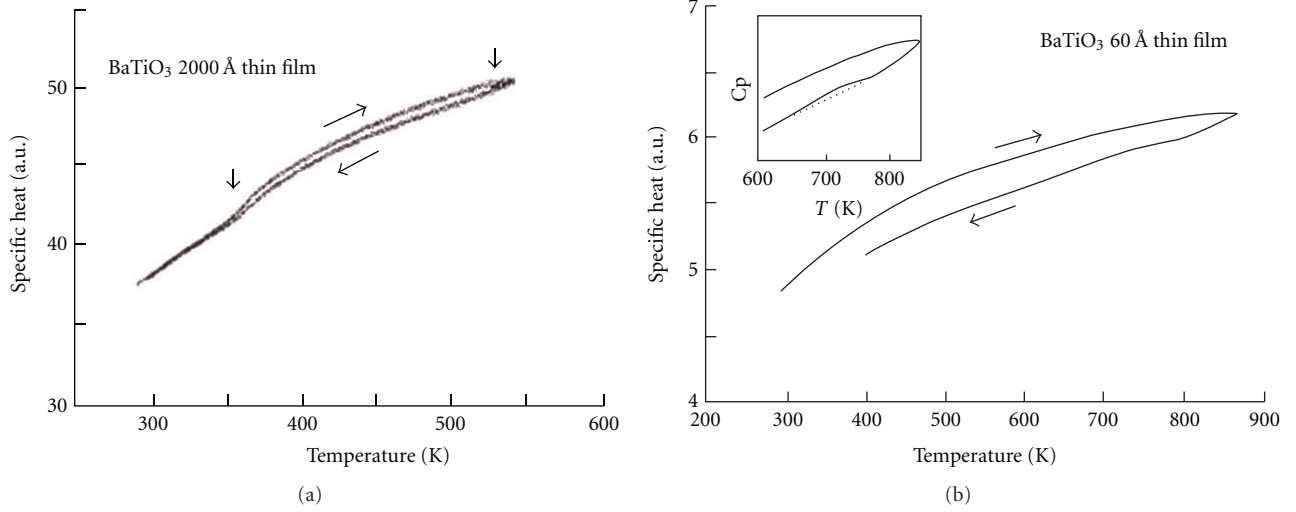
(a)

(b)

FIGURE 5: Temperature dependence of specific heat of $BaTiO_3$ epitaxial thin films on $SrTiO_3$ substrate; (a) 2000 Å thick and (b) 60 Å thick. The arrows show the direction of heating and cooling. The sharp anomalous specific heat in the single crystal changes to diffuse one in thin films [21].
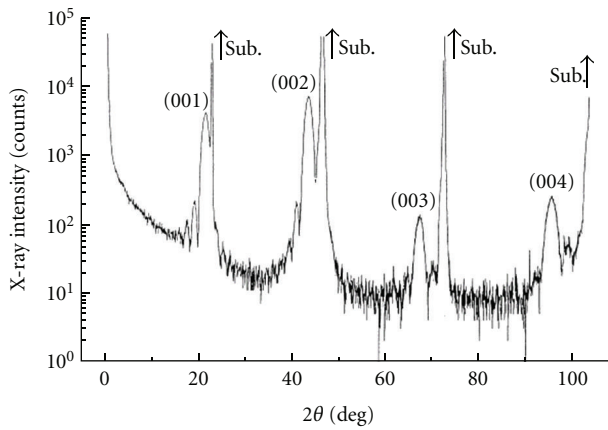

FIGURE 6: X-ray diffraction profiles along the [0 0 l] direction of the $BaTiO_3$ thin films with 60 Å on $SrTiO_3$ substrate (monochromatized CuKα). Subscript "Sub" means reflections from $SrTiO_3$ substrate [24].

TABLE 1: Positional and thermal parameters of ferroelectric phase ($A2_1am$) of $SrBi_2Ta_2O_9$ at 300 K [25].

Atom	x	y	z	B_{eq}
Sr	0	0.2610	0	0.69 (1)
Bi	0.4833 (14)	0.7738 (4)	0.2011 (1)	1.77 (1)
Ta	0.5177 (16)	0.7468 (6)	0.4143 (1)	0.37 (1)
O(1)	0.5365 (89)	0.3335 (67)	0	1.04 (5)
O(2)	0.4904 (72)	0.7316 (49)	0.3402 (4)	1.55 (4)
O(3)	0.7057 (76)	0.0146 (130)	0.2623 (5)	0.85 (4)
O(4)	0.7523 (94)	0.0002 (101)	0.0730 (6)	0.62 (5)
O(5)	0.7854 (87)	0.9744 (93)	0.5850 (6)	0.91 (4)

(a)   (b)
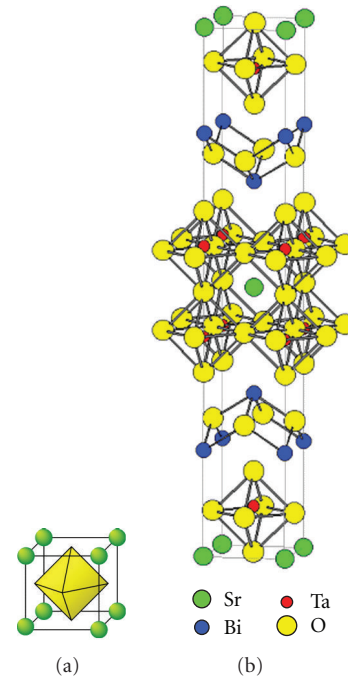
FIGURE 7: Crystal structure of (a) fundamental perovskite and (b) Bi-layered perovskite $SrBi_2Ta_2O_9$ (upper half of the unit cell) [11, 25].

the a axis normal to the pseudo-tetragonal axis, while along the tetragonal c axis in $BaTiO_3$. The crystal structure is highly anisotropic along the pseudo-tetragonal c axis and the single crystal of SBT has easily cleaved along the pseudo-tetragonal c axis, as the semiconducting Bi_2O_2 layer connects weakly upper and lower perovskite groups by van der Waals interaction. Crystal structure analysis of SBT shows that TaO_6
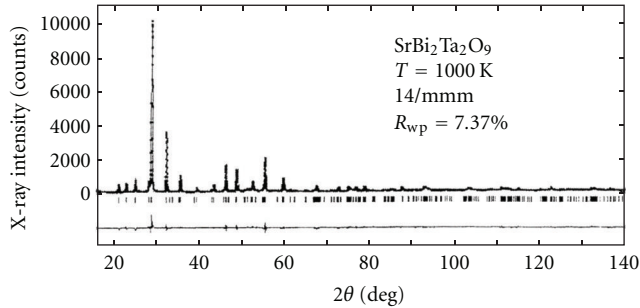
FIGURE 8: X-ray diffraction patterns of $SrBi_2Ta_2O_9$ ($CuK\alpha$) at 1000 K [25].

TABLE 2: Positional and thermal parameters of the paraelectric phase (I4/mmm) $SrBi_2Ta_2O_9$ at 1000 K [25].

Atom	x	y	z	B_{eq} (A)
Sr	0	0	0	1.09 (1)
Bi	0	0	0.2007 (1)	3.41 (1)
Ta	0	0	0.4140 (1)	0.05 (1)
O(1)	0	0.5	0.25	0.8 (6)
O(2)	0	0	0.5	1.41 (5)
O(3)	0	0.5	0.0756 (3)	0.75 (4)
O(4)	0	0	0.3479 (5)	1.17 (4)

FIGURE 9: Ferroelectric correlation region in dipolar materials [28].

octahedra are still distorted along the pseudo-tetragonal c axis, and locate in antiparallel way even in the high-temperature paraelectric phase above 850 K. Although the -O-Ta-O-Ta-O- chain along the pseudo-tetragonal c axis is interrupted by the existence of semiconducting Bi_2O_2 layers, this evidence indicates the strong interaction to displace along the c axis exists and the strongly correlated -O-Ta-O-Ta-O- chain should play an essential role for the appearance of ferroelectricity in SBT as those in $BaTiO_3$ [26]. In the high-temperature paraelectric phase, total polarization cancels by the antiparallel arrangement of octahedra, since TaO_6 is not perfect octahedron but elongates along the c axis; this indicates SBT is antiferroelectric above 850 K. In the ferroelectric phase, this crystal favors canted octahedral arrangements below T_c, which results in the net spontaneous polarization along the a axis. As this situation is just the same as those reported in the case of weak ferromagnetism in magnetic materials, we suggest canted ferroelectricity (weak ferroelectricity) for SBT.

On the other hand, this pseudo-two-dimensional character of crystal structure is just suitable for fabrication of thin films. The spontaneous polarization (P_s) is relatively large ($5.8 \sim 10\,\mu C/cm^2$ along the a axis at room temperature), while $P_s = 26\,\mu C/cm^2$ in a representative perovskite ferro-electric $BaTiO_3$ along the tetragonal c axis.

It should be noticed that these two perovskite oxides exhibit quite different dielectric nature. However, it is very interesting to point out the similarity in dielectric properties between $BaTiO_3$ thin films and SBT bulk crystals, since $BaTiO_3$ thin ferroelectric films exhibit diffuse dielectric anomaly.
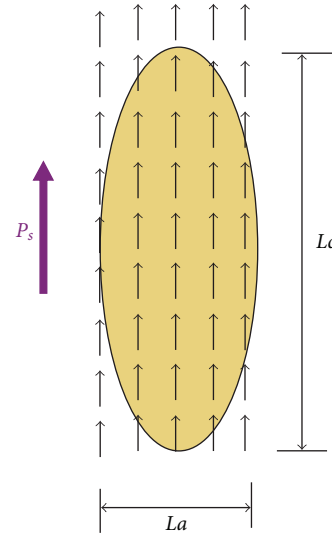
5. Size Effect in Ferroelectric Thin Films

Ferroelectricity appears due to a delicate balance between long-range dipole-dipole interaction along the polar axis and short-range interaction. The typical dipolar correlation lengths for many ferroelectrics are $Lc = 100 \sim 500\,\text{Å}$ along the polar axis and $La = 10 \sim 20\,\text{Å}$ normal to the polar axis [28]. The needle-shaped correlation region is sketched in Figure 9, where La is several unit cells, of the same order as the thickness of a 180° domain wall, and Lc is about $25 \sim 125$ unit cells in the case of $BaTiO_3$. Therefore, it should be reasonable to consider that the stability of the ferroelectricity may be suppressed by decreasing the thickness of the thin films.

Measurements of thickness dependence of ferroelectricity are generally not so easy, because of difficulties in preparation of good quality of thin films, and additional surface effects such as depolarization fields, space-charge effects, and misfit strain between film and substrate. These effects essentially influence the ferroelectric behavior in thin films. Many attempts have been reported to study the thickness dependence of ferroelectric properties of ferroelectric thin films prepared by vacuum evaporation, sputtering techniques, chemical vapor deposition, and so on.

Tybell, Ahn, and Triscone have examined the possibility of the existence of a critical thickness and showed the detection of the ferroelectricity in perovskite $Pb(Zr_{0.2}Ti_{0.8})_3$ films down to a thickness of 10 unit cells (40 Å) [37]. Bune et al. reported ferroelectric activity in ferroelectric polymer films with thickness of two layers (10 Å) and the near absence of finite-size effects in these two-dimensional ferroelectrics which may be generated by coupling only within the plane of the film [38]. Recent *Ab initio* studies have confirmed the possibility of retaining the ferroelectricity in ultra-thin films, and suggested the absence of the critical size effect [39, 40].

On the other hand, Junquera and Ghosez reported first-principle calculations on a realistic model of perovskite thin

TABLE 3: Estimated dipole moment of TaO_6 octahedron of the ferroelectric phase at 300 K ($A2_1am$) and the high-temperature paraelectric phase (I4/mmm) at 1000 K [25].

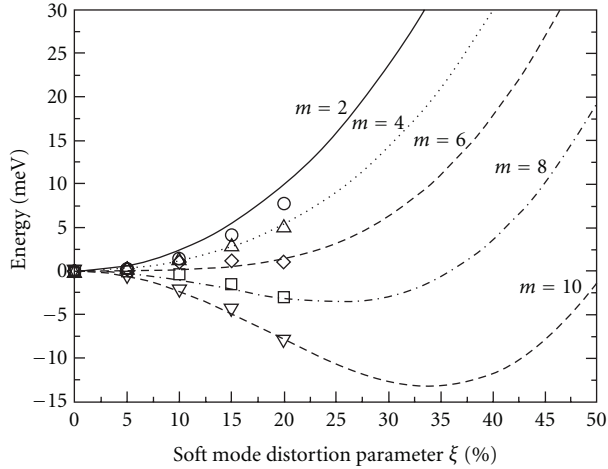|	A2$_1$am				I4/mmm
	Present study	Miura [34]	Shimakawa et al. [35]	Rae et al. [36]	Present study
p_x	0.035	0.564	0.425	0.386	0
p_y	−0.702	−0.074	0.001	0.003	0
p_z	1.528	1.747	1.169	1.117	1.365
p	1.682	1.837	1.244	1.182	1.365

FIGURE 10: First-principles calculations of the energy of $BaTiO_3$ ferroelectric films with m unit cells as a function of the soft-mode distortion ξ [29].

FIGURE 11: The plot of the ferroelectric phase transition temperature T_c versus film thickness of $BaTiO_3$ films grown on $SrTiO_3$ substrates, observed by Raman scattering [30].

films with metallic electrodes. They showed that $BaTiO_3$ films with $SrRuO_3$ electrodes have the critical thickness of 6 unit cells (~24 Å) and lose the ferroelectricity below this thickness, due to the depolarization field effect at the ferroelectric-metal interfaces (Figure 10) [29].

Recent Raman scattering studies showed that ultra-thin $BaTiO_3$ films grown commensurately on $SrTiO_3$ substrates have a spontaneous polarization as thin as 4 unit cells (16 Å) [30]. The ferroelectric phase transition temperature T_c are shown as a function of $BaTiO_3$ film thickness in Figure 11. Recent experimental and theoretical works showed the critical thickness is much smaller than those previously reported.

6. Mechanism of Phase Transition in SBT

It should be pointed out the close analogy of ferroelectric behavior between Bi-layered perovskite $SrBi_2Ta_2O_9$ (SBT) and thin film of the so-called typical ferroelectric perovskite $BaTiO_3$. The crystal structures of the high-temperature paraelectric phase at 1000 K and the ferroelectric phase at r. t. are schematically shown in Figure 10 [25]. The TaO_6 octahedra are distorted in both phases. Even in the high-temperature paraelectric phase, the octahedra are elongated along the pseudo-tetragonal c axis and locate in an antiparallel way.
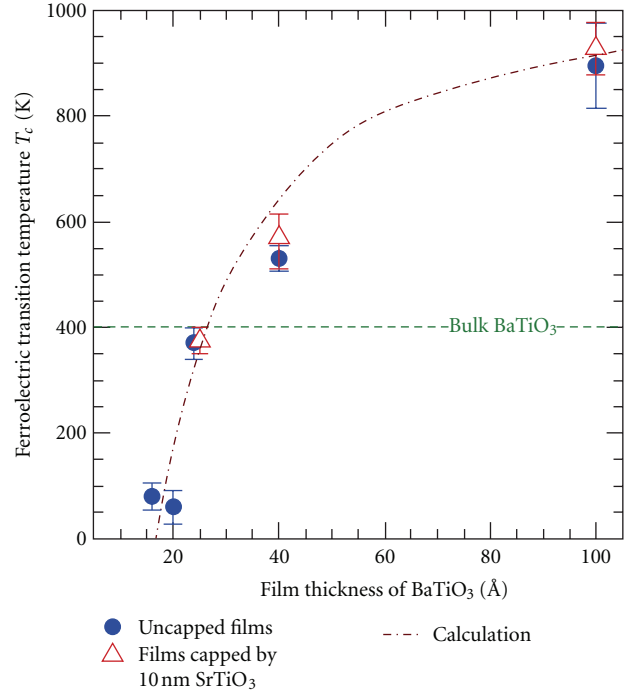
The distortion parameter of one TaO_6 octahedron, p, defined as

$$p = |\mathbf{p}| = \sum_{i=1}^{7} q_i(\mathbf{r}_i - \mathbf{r}_G), \qquad (3)$$

is estimated to be 1.365 debye along the c axis as shown in Table 3, where q_i and $\mathbf{r}_i$ are charge and position of each constituent ion, and $\mathbf{r}_G$ is the gravity center of TaO_6. The parameter $\mathbf{p}$ is obtained as (0, 0, 1.365) in debye unit in the high-temperature paraelectric phase. In the ferroelectric phase, the absolute value is 1.682 debye, which is almost the same as that of the high-temperature paraelectric phase within errors. If the distortion of octahedron corresponds to a dipole moment, it should be probable that SBT prefers an antiferroelectric structure along the c-axis, when the distorted octahedra are mainly responsible for the ferroelectric activity. Furthermore, these distorted octahedra have a canted arrangement in the ferroelectric phase as shown in Figure 12.
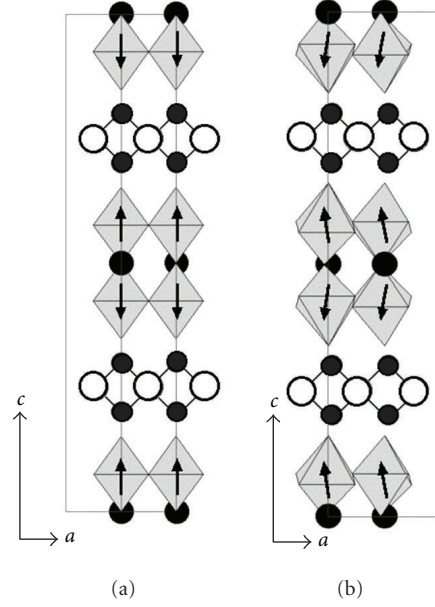
(a)　　　　　　　　　　　(b)

FIGURE 12: Crystal structures of (a) the paraelectric and (b) the ferroelectric phases of layered perovskite $SrBi_2Ta_2O_9$. Arrows show estimated dipole arrangements of TaO_6 octahedra [25].

These structural arrangements of TaO_6 octahedra in SBT remind us of a canted-ferromagnet (or weak ferromagnet) discussed by Moriya [41] and in layered canted-ferromagnets by de Gennes [42]. The free energy is given in terms of sublattice polarizations P_1, P_2, and an angle θ between them as

$$F = \frac{1}{2}\alpha_1 P_1^2 + \frac{1}{2}\alpha_2 P_2^2 + gP_1P_2\cos\theta - \delta P_1P_2\sin\theta, \quad (4)$$

where the third symmetrical term is a well-known exchange interaction and the last term is an antisymmetric Dzialoshinski-Moriya interaction. If $\theta = \pi$ and $\alpha_1 = \alpha_2$, the above expression is just the same as that for antiferroelectrics proposed by Kittel [43]. The last term favors the canted arrangement of dipoles rather than antiferroelectric one. From the condition, $\partial F/\partial\theta = 0$, we get the following relation:

$$\tan\theta = -\frac{\delta}{g}. \quad (5)$$

As the observed value of θ is $154°$, the coefficient δ of the antisymmetric term is about half of the symmetric one g. From the relations

$$\frac{\partial F}{\partial P_1} = \frac{\partial F}{\partial P_2} = E, \quad (6)$$

we have the expression for the dielectric susceptibility as

$$\chi = \frac{2}{(\alpha + g')}, \quad (7)$$

where

$$g' = g\cos\theta - \delta\sin\theta, \quad (8)$$

when we assume $\alpha_1 = \alpha_2 = \alpha$. It is evident that the dielectric susceptibility shows small anomaly just like antiferroelectric one, which may be smeared by two-dimensional surface strain as pointed out by Tagantsev et al. [19]. Because of the term of the Dzialoshinski-Moriya interaction, the ferroelectric phase transition will be realized in SBT, and the characteristic weak dielectric properties may be explained. The asymmetric interaction may be attributed to the two-dimensional effect in SBT and $BaTiO_3$ epitaxial thin films.

The decrease and nonclear behavior of dielectric constant were also observed around T_c with decreasing film thickness in $(Ba, Sr)TiO_3$ thin films. In this case, Hwang analyzed this decrease by considering the effects of a finite charge-screening length of metal electrodes and an intrinsic dead layer of the surface [44]. The layered ferroelectric SBT is a bulk crystal itself, and is considered to be an example of ultra-thin ferroelectric model with two perovskite layers, free from any misfit lattice strain and interface charge layer with electrodes.

It should be pointed out that the ferroelectricity of perovskite thin films with two unit cells may be stable even in those with $m = 2$, although its polarization does not appear along the tetragonal axis but along the axis normal to the tetragonal axis (within layer). Therefore, there is a crossover of ferroelectric to antiferroelectric interaction along the tetragonal axis, with decreasing the stacking number of perovskite units. Furthermore, the ultra-thin films prefer an antiferroelectric structure rather than a ferroelectric structure in thin films.

7. Soft Mode in Bi-Layered Perovskite

Measurements of the soft mode of SBT have been reported by Raman scattering as shown in Figure 13 [31, 32, 45].
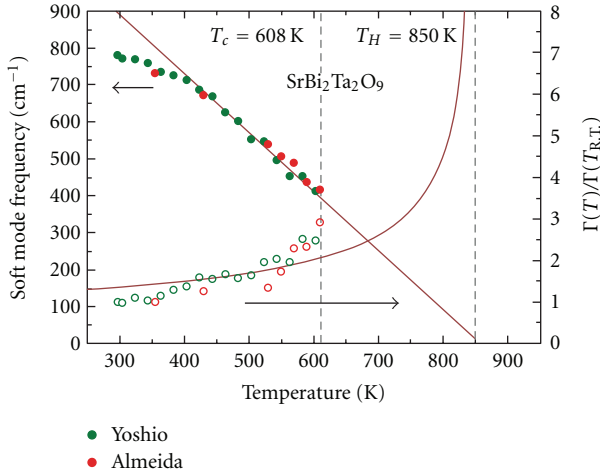
FIGURE 13: Temperature dependence of soft mode frequency (square of Raman frequency shift) and a normalized damping factor $\Gamma(T)/\Gamma(T_{R.T.})$ in $SrBi_2Ta_2O_9$ [31–33].

The square of soft mode frequency decreases toward the highest phase transition temperature (850 K) and shows a clear anomaly at 610 K (T_c). The soft mode exists in the ferroelectric phase and shows highly overdamped behavior near T_c, although dielectric constant does not diverse at T_c. Another anomaly was detected in the share strain c_{44} at 850 K [46], which corresponds to the high-temperature phase transition at 850 K.

A series of Bi-layered perovskites compounds $Bi_{2m}A_{n-m}B_nO_{3(n+m)}$ were synthesized by Aurivillius in 1949 [47]. As $Sr_2Bi_4Ti_5O_{18}$ is a compound with five perovskite layers with Bi_2O_2 semiconducting layers as shown in Figure 14, it is considered as a model of perovskite thin film with five unit cells. This crystal undergoes a ferroelectric phase transition at 558 K, although it has been reported that the ferroelectricity of thin films may be suppressed below six unit cells after Junquera and Ghosez [29]. In this compound, similar dielectric properties as those observed in SBT have been reported. The spontaneous polarization appears along the a axis and the dielectric constant shows rather weak temperature dependence. In $Sr_2Bi_4Ti_5O_{18}$, similar temperature dependence of soft mode was observed by Raman scattering [33]. Raman spectra showed two anomalies at 551 K and at 730 K. The soft mode frequency decreases toward 730 K, although it shows overdamped behavior over 450 K. Furthermore, two additional relaxation modes have been observed, which show an anomaly at 551 K. Even in the case of SBT ($m = 2$) and $Sr_2Bi_4Ti_5O_{18}$ ($m = 5$), the soft mode still exists, although it becomes highly overdamped near T_c.

8. Summary and Discussion

Bi-layered perovskites have been much attracted as a promising material for ferroelectric integrated devices. According to the calculations of local field by Luttinger and Tisza [48], the strong ferroelectric interaction between Ti (or Ta) ion and O ions appears along the tetragonal c axis. Although the
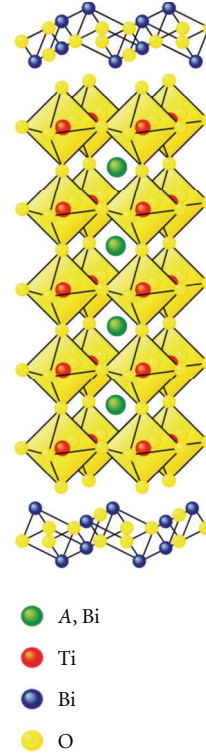

FIGURE 14: Crystal structure of Bi-layered perovskite $A_2Bi_4Ti_5O_{18}$ with $m = 5$.

strongly correlated -O-Ti-O-Ti-O- chain plays an important role for the appearance of ferroelectricity in bulk $BaTiO_3$ [26], the -O-Ta-O-Ta-O- chain along the pseudo-tetragonal c axis is interrupted by the existence of semiconductor Bi_2O_2 layers in SBT. The strength of interaction between Ti ion and adjacent O ions is half, but antiferroelectric in the a-b plane. However, the configuration of distortion parameter p in Figure 12 suggests us that the interaction is strong but antiferroelectric along the pseudotetragonal c axis, and ferroelectric along the a axis in SBT. It is expected that a crossover of ferroelectric to antiferroelectric interaction will be realized even in thin films of $BaTiO_3$, considering the similarity of dielectric properties between SBT bulk crystal and thin $BaTiO_3$ films mentioned above. In this sense, SBT bulk crystals may be considered as a model of ferroelectric thin films. It might be expected that the cant of dipole moments may be induced even in thin $BaTiO_3$ films by the two-dimensionality.

The suppression of ferroelectricity has been reported for nano-particles of $BaTiO_3$ and $PbTiO_3$, where the critical size is $20 \sim 30$ unit cells [49]. However, the dipole-dipole interactions within plane are retained and contribute to ferroelectric activity in the case of thin films.
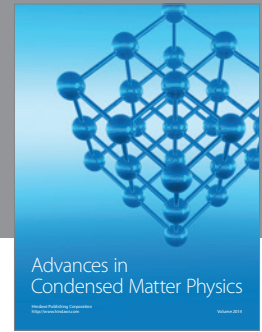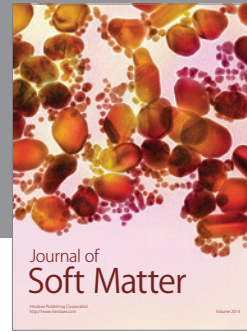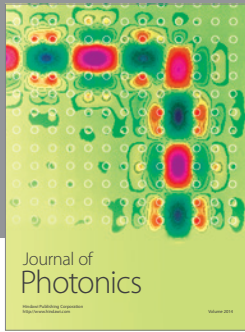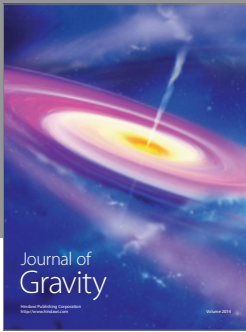
The dielectric and structural analogy between $SrBi_2Ta_2O_9$ and thin film suggests that this bulk layered ferroelectric is a good model of ultra-thin ferroelectric films with two layers of TaO_6 perovskite units, free from any misfit lattice strain with substrate and surface charge at the interface with electrodes. In perovskite ultra-thin films, ferroelectric

interactions are still prominent and the octahedra prefer an antiferroelectric arrangement rather than ferroelectric one along the tetragonal axis (normal to the plane) in the case of two layers. The soft mode exists but changes to be highly over damped near the ferroelectric phase transition temperature. Moreover, the mechanism mentioned above might be applicable for $Sr_2Bi_4Ti_5O_{18}$ with five perovskite groups ($m = 5$), because the almost same dielectric behavior has been observed in $Sr_2Bi_4Ti_5O_{18}$ which has perovskite units less than six unit cells. Further experiments will be necessary both in layered oxide ferroelectrics and perovskite thin films.

References

[1] W. Cochran, "Crystal stability and the theory of ferroelectricity," *Advances in Physics*, vol. 9, pp. 387–423, 1960.

[2] W. Cochran, "Crystal stability and the theory of ferroelectricity part II. Piezoelectric crystals," *Advances in Physics*, vol. 10, pp. 401–420, 1961.

[3] C. A.-P. de Marajo, J. D. Cushier, L. D. McMillan et al., "Fatigue-free ferroelectric capacitors with platinum electrodes," *Nature*, vol. 374, pp. 627–629, 1995.

[4] J. F. Scott, "NANO-phase SBT-family ferroelectric memories," *Ferroelectrics Review*, vol. 1, pp. 1–14, 1998.

[5] M. Dauber, K. M. Raba, and J. F. Scott, "Physics of thin-film ferroelectric oxides," *Reviews of Modern Physics*, vol. 77, pp. 1083–1130, 2005.

[6] G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, "Ferroelectrics of the oxygen-octahedral type with layered structure," *Soviet Physics*, vol. 3, no. 3, pp. 651–655, 1961.

[7] Y. Yoneda, H. Kasatani, H. Terauchi, Y. Yano, T. Terashima, and Y. Bando, "Ferroelectric phase transition in $BaTiO_3$ films," *Journal of the Physical Society of Japan*, vol. 62, no. 6, pp. 1840–1843, 1993.

[8] K. Yoshio, A. Onodera, and H. Yamashita, "Ferroelectric phase transition and new intermediate phase in Bi-layered perovskite $SrBi_2Ta_2O_9$," *Ferroelectrics*, vol. 284, no. 1, pp. 65–74, 2003.

[9] E. C. Subbarao, "A family of ferroelectric bismuth compounds," *Journal of Physics and Chemistry of Solids*, vol. 23, no. 6, pp. 665–676, 1962.

[10] A. Onodera, K. Yoshio, C. C. Myint, S. Kojima, H. Yamashita, and T. Takama, "Thermal and structural studies of phase transitions in layered perovskite $SrBi_2Ta_2O_9$," *Japanese Journal of Applied Physics B*, vol. 38, no. 9, pp. 5683–5685, 1999.

[11] A. Onodera, T. Kubo, K. Yoshio, S. Kojima, H. Yamashita, and T. Takama, "Crystal structure of high-temperature paraelectric phase in Bi-layered perovskite $Sr_{0.85}Bi_{2.1}Ta_2O_9$," *Japanese Journal of Applied Physics B*, vol. 39, no. 9, pp. 5711–5715, 2000.

[12] A. Onodera, K. Yoshio, C. C. Myint et al., "Thermal behavior in ferroelectric $SrBi_2Ta_2O_9$ thin films," *Ferroelectrics*, vol. 241, pp. 159–166, 2000.

[13] W. Murata, A. Onodera, K. Yoshio et al., "Ferroelectric phase transition in layered perovskite $SrBi_2Ta_2O_9$," *Ferroelectrics*, vol. 270, no. 1, pp. 303–308, 2002.

[14] A. Onodera, K. Yoshio, and H. Yamashita, "Structural study of intermediate phase in layered perovskite $SrBi_2Ta_2O_9$ single crystal," *Japanese Journal of Applied Physics*, vol. 42, pp. 6218–6221, 2003.

[15] H. Terauchi, Y. Yoneda, Y. Watanabe et al., "Epitaxial $BaTiO_3$ crystals," *Ferroelectrics*, vol. 151, no. 1, pp. 21–26, 1994.

[16] Y. Yoneda, H. Kasatani, H. Terauchi, Y. Yano, T. Terashima, and Y. Bando, "Ferroelectric phase transition in $BaTiO_3$ films," *Journal of Crystal Growth*, vol. 150, no. 1, pp. 1090–1093, 1995.

[17] K. Iijima, T. Terashima, Y. Bando, K. Kamigaki, and H. Terauchi, "Atomic layer growth of oxide thin films with perovskite-type structure by reactive evaporation," *Journal of Applied Physics*, vol. 72, no. 7, pp. 2840–2845, 1992.

[18] Y. Yano, K. Iijima, Y. Daitoh et al., "Epitaxial growth and dielectric properties of $BaTiO_3$ films on Pt electrodes by reactive evaporation," *Journal of Applied Physics*, vol. 76, no. 12, pp. 7833–7838, 1994.

[19] A. K. Tagantsev, N. A. Pertsev, P. Muralt et al., "Strain-induced diffuse dielectric anomaly and critical point in perovskite ferroelectric thin films," *Physical Review B*, vol. 65, Article ID 012104, 4 pages, 2001.

[20] S. Grabovsky, M. Takesada, A. Onodera et al., "Specific heat and light scattering data of barium titanate crystals near ferroelectric phase transition," in *Abstract of Annual Meeting of Physical Society of Japan*, Kansei-Gakuin University, March 2012.

[21] A. Onodera, Y. Kawamura, T. Okabe, and H. Terauchi, "Specific heat in ferroelectric $BaTiO_3$ epitaxial thin films," *Journal of the European Ceramic Society*, vol. 19, no. 6-7, pp. 1477–1480, 1999.

[22] B. A. Strukov, S. T. Davitadze, S. A. Taraskin et al., "Thermodynamical properties of the thin polycrystalline $BaTiO_3$ films on substrates," *Ferroelectrics*, vol. 286, pp. 245–250, 2003.

[23] S. T. Davitadze, S. N. Kravchun, B. A. Strukov, B. M. Goltzman, V. V. Lemanov, and S. G. Shulman, "Specific heat and thermal conductivity of $BaTiO_3$ polycrystalline thin films," *Applied Physics Letters*, vol. 80, no. 9, pp. 1631–1633, 2002.

[24] H. Terauchi, Y. Watanabe, H. Kasatani et al., "Structural study of epitaxial $BaTiO_3$ crystals," *Journal of the Physical Society of Japan*, vol. 61, no. 7, pp. 2194–2197, 1992.

[25] H. Yamashita, K. Yoshio, W. Murata et al., "Structural changes and ferroelectricity in bi-layered $SrBi_2Ta_2O_9$," *Japanese Journal of Applied Physics*, vol. 41, pp. 7076–7079, 2002.

[26] J. C. Slater, "The lorentz correction in barium titanate," *Physical Review*, vol. 78, pp. 748–761, 1950.

[27] H. Terauchi, Y. Watanabe, H. Kasatani et al., "X-Ray studies on single crystal films of $BaTiO_3$," *Ferroelectrics*, vol. 137, pp. 33–38, 1992.

[28] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, UK, 1977.

[29] J. Junquera and P. Ghosez, "Critical thickness for ferroelectricity in perovskite ultrathin films," *Nature*, vol. 422, no. 6931, pp. 506–509, 2003.

[30] D. A. Tenne, P. Turner, J. D. Schmidt et al., "Ferroelectricity in ultrathin $BaTiO_3$ films: probing the size effect by ultraviolet raman spectroscopy," *Physical Review Letters*, vol. 103, no. 17, Article ID 177601, 2009.

[31] K. Yoshio, I. Matsubara, A. Yamada et al., "Phase transition in ferroelectric $SrBi_2Ta_2O_9$ single crystal," *Journal of Korean Physics Society*, vol. 43, p. S1034, 2003.

[32] A. Almeida, M. R. Chaves, H. Amorin, M. E. V. Costa, and A. L. Kholkin, "Lattice dynamics study of high-quality strontium bismuth tantalate single crystals," *Journal of Physics Condensed Matter*, vol. 17, no. 48, pp. 7605–7612, 2005.

[33] M. Fukunaga, "Soft mode and relaxation behavior in two-dimensional ferroelectric Bi-layered perovskites," *[Ph.D. thesis]*, HokkaidoUniversity, 2009.

[34] K. Miura, "Electronic properties of ferroelectric $SrBi_2Ta_2O_9$, $SrBi_2Nb_2O_9$, and $PbBi_2Nb_2O_9$ with optimized structures," *Applied Physics Letters*, vol. 80, p. 2967, 2002.

[35] Y. Shimakawa, Y. Kubo, Y. Nakagawa et al., "Crystal structures and ferroelectric properties of $SrBi_2Ta_2O_9$ and $Sr_{0.8}Bi_{2.2}Ta_2O_9$," *Applied Physics Letters*, vol. 74, p. 1904, 1998.

[36] A. D. Rae, J. G. Thompson, and R. L. Withers, "Structure refinement of commensurately modulated bismuth strontium tantalate, $Bi_2SrTa_2O_9$," *Acta Crystallographica B*, vol. 48, pp. 418–428, 1992.

[37] T. Tybell, C. H. Ahn, and J. M. Triscone, "Ferroelectricity in thin perovskite films," *Applied Physics Letters*, vol. 75, no. 6, pp. 856–858, 1999.

[38] A. V. Bune, V. M. Fridkin, S. Ducharme et al., "Two-dimensional ferroelectric films," *Nature*, vol. 391, no. 6670, pp. 874–877, 1998.

[39] B. Meyer and D. Vanderbilt, "Ab initio study of $BaTiO_3$ and $PbTiO_3$ surfaces in external electric fields," *Physical Review B*, vol. 63, Article ID 205426, 2001.

[40] Ph. Ghosez and K. M. Rabe, "Microscopic model of ferroelectricity in stress-free $PbTiO_3$ ultrathin films," *Applied Physics Letters*, vol. 76, p. 2767, 2000.

[41] T. Moriya, "Weak ferromagnetism," in *Magnetism*, G. T. Rado and H. Suhl, Eds., vol. 1, p. 85, Academic Press, New York, NY, USA, 1963.

[42] P.-G. de Gennes, "Effects of double exchange in magnetic crystals," *Physical Review B*, vol. 118, pp. 141–154, 1960.

[43] C. Kittel, "Theory of antiferroelectric crystals," *Physical Review*, vol. 82, pp. 729–732, 1951.

[44] C. S. Hwang, "Thickness-dependent dielectric constants of $(Ba,Sr)TiO_3$ thin films with Pt or conducting oxide electrodes," *Applied Physics*, vol. 92, p. 432, 2002.

[45] J.-H. Ko, A. Hushur, S. Kojima et al., "Acoustic anomalies and central peak in $SrBi_2Ta_2O_9$ single crystals studied by micro-Brillouin scattering," *Applied Physics Letters*, vol. 81, p. 4043, 2002.

[46] M. Takesada, K. Sutoh, M. Fukunaga, and A. Onodera, "Light scattering study of bismuth layered ferroelectric $SrBi_2Ta_2O_9$," *Ferroelectrics*, vol. 355, no. 1, pp. 149–153, 2007.

[47] B. Aurivillius, "Mixed bismuth oxides with layer lattices I. The structure type of $CaNb_2Bi_2O_9$," *Arkkitehtuuritoimisto*, vol. 1, p. 893, 1949.

[48] J. M. Luttinger and L. Tisza, "Theory of dipole interaction in crystals," *Physical Review*, vol. 72, no. 3, p. 257, 1947.

[49] K. Ishikawa, T. Nomura, N. Okada et al., "Size effect on the phase transition in *PbTiO*3 fine particles," *Japanese Journal of Applied Physics*, vol. 35, pp. 5196–5198, 1996.