Study the Crystal Structure and Phase Transition of BaTiO$_3$ – A Pervoskite

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Abstract: Perovskites belong to one of the largest oxide families. The interesting physical properties and important applications have been widely investigated in this system since the last century. Among the large perovskite family, one of the most important groups is the ferroelectric oxide, which possesses extremely high values of dielectric constant and low dielectric loss, as well as good dielectric tunability. Ferroelectricity has been known since the 1920s and ferroelectricity in perovskite BaTiO$_3$ (BTO) was first discovered in the 1940s. In the present work we have studied the pervoskite nature of BaTiO$_3$ (BTO) with its Crystal structure and phase transition.

Introduction

Historically, ferroelectric materials have been investigated and practically applied mainly in their bulk form. However, in the last 20-25 years, more and more applications call for a continual reduction in size, and require a thin film implementation. It generally requires a film layer thinner than 1 μm, which brings a lot of new challenges in manufacture and application. Some of the challenges come from the fact that the area of surfaces and interfaces is very large compared to the volume of the thin film, while in bulk materials their importance is often negligible. Due to the restricted geometry, grain boundaries, dislocations, inclusions and all other defects have entirely different behavior compared to the bulk materials, and therefore resulting the properties of thin films are markedly different from those of their bulk counterparts. Novel and effective deposition methods for thin films have been widely investigated during last decade. However, the deposition and film growth mechanisms and the produced microstructures that dedicate the resulting properties are still not very clear. In addition, the large stresses in the film, which could result from the film growth, thermal expansion coefficient mismatches during integration and operation, could alter the Curie temperature and change the ferroelectric phase transitions. A comprehensive understanding of the growth mechanism and interface effect for the ferroelectric thin film is therefore essential to fully make use of the unique properties of these interesting materials.

Perovskite epitaxial oxide thin films possess various novel properties, such as high dielectric constant; good ferroelectric properties; low dielectric loss, and are considered as one of the most important material families to meet challenges in advanced material research and nanotechnology. In the large perovskite oxide families, BTO is one of the most attractive functional materials in the electronics industry, due to its superior dielectric, ferroelectric, piezoelectric, and electro-optical properties [1-4]. BTO thin films have been considered as promising materials for many device applications such as ferroelectric random access memories, optical modulators and switches, waveguides and micro-electromechanical systems [5-8].

Partially substituted BTO thin films have been widely investigated since the dramatic change in physical properties, caused by small amount of substitution. Substituting Ba^{2+} by Sr^{2+} in BaTiO$_3$, (Ba,Sr)TiO$_3$ (BST) thin films has been found to possess high dielectric constant, relatively low dielectric loss tangent and large electric field tunability and have attracted considerable attention for dynamic random access memories (DRAM), capacitors, detectors, and tunable microwave applications [9,10].With Ti^{4+} partially substituted by Zr^{4+} in BaTiO$_3$, Ba(Zr,Ti)O$_3$ (BZT) films exhibit high tunability and low loss, which has shown the promise for tunable filters, phase shifter, antennas, etc [11,12]. It is well known that the fabrication of highly epitaxial oxide thin films requires a good understanding of the effects of growth conditions, material parameters and the film/substrate interfacial structures on the epitaxial behavior. And also the physical properties of epitaxial thin films are strongly determined by the microstructure including crystallographic structure, corresponding orientation, domains, and boundaries of the epitaxial films, and the interface between the film and substrate. Especially, the lattice mismatch at the interface can largely control the epitaxial behavior and film microstructure [13-15], and significantly change the physical properties, such as Curie temperature, magnetic properties, and dielectric properties [16-18]. Thus, the partial substitutions and interface structure between the film and substrate have a critical influence on the microstructure of epitaxial thin films. Therefore, in this

dissertation, the study of interface effect and doping effect on barium titanate based ferroelectric oxide thin films become essential. The fundamental investigation and development of these effects on the film growth mechanism become more important to develop an understanding of the relationship between microstructure and properties for thin films.

Pervoskite Structure

"Perovskite" was initially the name of the mineral perovskite $CaTiO_3$; however more generally represents the large structural family of compounds having crystal structures related to perovskite $CaTiO_3$. Ideally, the crystal structure of perovskites can be described as ABX_3. X is often oxygen but also other large ions such as F^- and Cl^- are possible. The ABX_3 perovskite structure stands out by a wide margin compared with other structures, since it can produce an incredibly wide array of phases with totally different functions with various chemical manipulations, as shown in Figure 1. In this family, the perovskite group of oxides with the chemical formula of ABO_3 is probably the best studied group of oxides. It can be visualized as a simple cubic unit cell with large cations A located at eight corners, smaller cations B sitting in the body center, and oxygen atoms in the face center, as shown in Figure 2 (a). The resulting perovskite structure can also be described as consisting of corner sharing $[BO_6]$ octahedra with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedral, as shown in Figure 2 (b) [19,20].
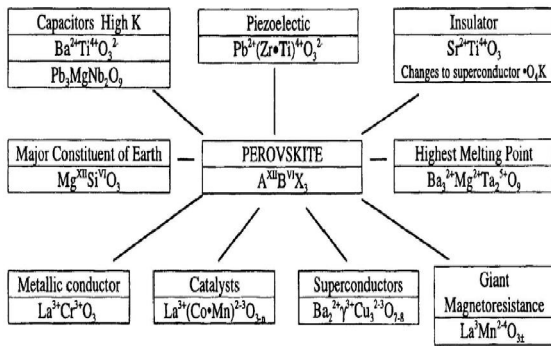

Figure 1 Perovskite-the maximum multifunctional structure

The ideal cubic perovskite structure is not very common and also the mineral perovskite itself is slightly distorted. The interest in compounds belonging to this family of crystal structures arise in the large and ever surprising variety of properties exhibited and the flexibility to accommodate almost all of the elements in the periodic system. The first structural study on perovskites we can find from literature, were conducted by Goldschmidt *et al* in the 1920s that formed the basis for further exploration of the perovskite family of oxides

[21]. The distortion of the $[BO_6]$ octahedra due to temperature changes or stress effects may cause the transition from cubic structure to tetragonal, rhombohedral or orthorhombic structures. Distorted perovskites have reduced symmetry, which is important for their magnetic and electric properties. Due to these properties, perovskites have great industrial importance and huge potential for cutting edge technology, especially the ferroelectric pseudo-cubic barium titanate, $BaTiO_3$.

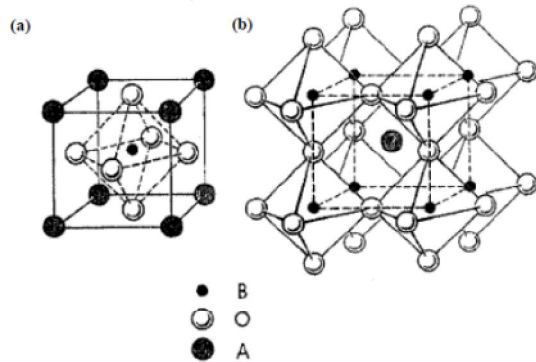Figure 2: ABO_3 perovskite crystal structure

In the cubic ABO_3 perovskite structure, the A atoms are in Wyckoff position 1b, ½,½,½; the B atoms in 1a, 0,0,0; and the X atoms in 3d ½,0,0; 0,½,0; 0,0,½, all special positions. If the position of the A^{2+} ion is vacant the remaining framework is that of the ReO_3 type. Partial occupation of the A position occurs in the cubic tungsten bronzes A_xWO_3 (A = alkali metal, $0.3 \leq x \leq 0.93$). The ReO_3 structure type can be converted to a more dense packing by rotating the octahedra until a hexagonal close packing is obtained of the RhF_3 type. The void in the center has then an octahedral surrounding. If this octahedral hole is occupied, then the structure of $FeTiO_3$ is formed. The perovskite structure is known to be very flexible and the A and B ions can be varied leading to the large number of known compounds with perovskite or related structures. Most perovskites are distorted and do not have the ideal cubic structure. Three main factors are identified as being the possible reason for the distortion in perovskite structure: size effects of atoms, deviations from ideal composition and the Jahn-Teller effect [22]. It is hard to distinguish that a distortion of a certain perovskite oxide can be assigned to a single effect. In most cases, several factors could act together on the structure.

(1) Size Effects

In the ideal cubic case, the cell axis, *a*, is geometrically related to the ionic radii (r_A, r_B, and r_O) as described in equation (1)

$$a = \sqrt{2}\,(r_A + r_0) = 2(r_B + r_0)$$

$$(1)$$

The ratio of the two expressions for the cell length is called the Goldschmidt's tolerance factor t. Based on the ionic radii (simply ionic bonding is assumed), t can be used to estimate the degree of distortion. However, when the compound with a high degree of ionic bonding is considered, another equation is addressed as equation (2):

$$t = \frac{(r_A + r_0)}{\sqrt{2}(r_B + r_0)}$$

$$(2)$$

If the A ion is smaller than the ideal value, then t becomes smaller than 1. As a result, the $[BO_6]$ octahedra will tilt in order to fill the space. However, in some cases the distortion of the cubic structure occurs if $0.89 < t < 1$ [23, 24]. One ideal example is cubic perovskite $SrTiO_3$, it has $t=1.00$, $r_A=1.44$ Å, $r_B=0.605$ Å, and $r_O=1.40$ Å. Lower values of t will reduce the symmetry of the crystal structure. For example $GdFeO_3$ with $t = 0.81$ is orthorhombic ($r_A = 1.107$ Å and $r_B = 0.78$ Å) [40]. Also, the mineral perovskite, $CaTiO_3$, has the structure with t less than 0.8, and therefore, the ilmenite structure is more stable for itself [25]. On the other hand if t is larger than 1, when a large A or a small B ion is referred, then the hexagonal structure for the perovskites is more stable, *e.g.* $BaNiO_3$ type structures. The t value for $BaNiO_3$ is 1.13 ($r_A = 1.61$ Å and $r_B = 0.48$ Å). In this case the closest packing layers are stacked in a hexagonal manner in contrast to the cubic one in $SrTiO_3$ structure, leading to face sharing of the $[NiO_6]$ octahedra. However, since perovskites are not truly ionic compounds and since the t values also depend on what values are taken for the ionic radii, the tolerance factor only can give a rough estimation for crystal structure.

(2) Composition Effects

Perovskite lattice could accommodate a great variety of metallic ions if the size and valence are compatible. The solid solution limit is significantly lower with ions of a different valence from the one replaced, presumably because of the excessive lattice vacancies that result. In Perovskites, because of the packing density, the presence of interstitial ions appears unlikely but substantial concentrations of A-site vacancies can be tolerated. There is not obvious evidence of the existence of any significant concentration of vacancies in B position of any perovskite [26, 27]. Compositions with stoichiometry that might yield a perovskite with B-site vacancies crystallize instead as a mixture of perovskite and nonperovskite phases.

An example is the family of compounds $SrFeO_x$ ($2.5 \leq x \leq 3$). The valency of the Fe ions can be changed by heating a sample in either an oxidizing or a reducing environment. As a result the oxygen content can vary in between 2.5 and 3. For the $SrFeO_{2.875}$ some Fe ions can be assigned to the oxidation state 3+ and 4+, therefore FeO_5 square pyramids are formed.

(3) Jahn-Teller Effects

The Jahn-Teller effects, sometimes also known as Jahn-Teller distortion, or the Jahn-Teller theorem. It is named after Hermann Arthur Jahn and Edward Teller, who proved that non linear spatially degenerate molecules cannot be stable [28]. The peculiarity of the Jahn-Teller interaction is that there must be a multiplicity of electronic states interacting with one or more normal modes of vibration, and the Jahn-Teller effect describes that for almost any set of degenerate electronic states associated with a molecular configuration, there will exist some symmetry-breaking interaction in which molecular distortion is associated with the removal of the electronic degeneracy. That is because the distortion can lower the overall energy of the complex. In some perovskites the distortion of the structure can be assigned to Jahn – Teller active ions at the B position. For example, in $LnMnO_3$ (Ln = La, Pr or Nb) with Mn^{3+} ions the 3d4 electrons divide up into 3 t_g and 1 e_g electron. The odd number of electrons in the e_g orbital causes an elongation of the $[MnO_6]$ octahedron. As a result, the perovskite structure has a wide range of substitution of cations A and B, as well as the anions. The principles of substitution must maintain charge balance and keep sizes within the range for particular coordination number. Since the variation of ionic size and composition, which result in the distortion of the structure and the reduction of symmetry, have tremendous effects on the physical properties of perovskite structure materials.

Barium Titanate (Structure)

Barium titanate is used in a variety of electronic applications due to its excellent ferroelectric properties with high dielectric constant, low dielectric loss; and its chemical and mechanical stability. Barium titanate is one of the most investigated ferroelectric materials due to its history as the first oxide ferroelectric, simple crystallographic structure and wide spread use in the electronic, optical and communications industry. The current technology advancement imposes an ever-increasing demand of development of new ferroelectric materials and improved materials performance. Barium titanate and barium titanate based materials have become one of the most promising ferroelectric materials to meet all those practical demands.

Crystal Structure and Phase Transition

Barium titanate, BaTiO₃, the first ceramic material from which ferroelectric behavior was observed, has a typical perovskite (ABO₃) structure. It has been one of the best Pb-free ferroelectric materials for microelectronic devices applications in perovskite oxide families and also an ideal model for discussing of the ferroelectricity and spontaneous polarization from the point of view of crystal structure. The idealized cubic structure can be realized in BaTiO₃ above the Curie temperature. Unlike many other oxide crystals, oxygen anions in perovskite do not form a close packing structure. Barium ions (A ions), which are large in size (~158 pm), occupy the corner sites, titanate ions (B ions), which are small in size (~60 pm), locate in the centers of the cube (the oxygen octahedral) and oxygen anions are on the face-centers.
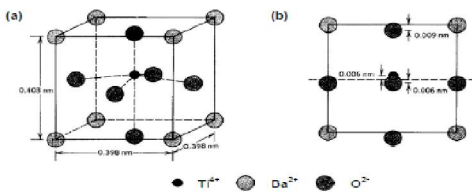

Figure 3 (a) A barium titanate (BaTiO₃)

At the Curie temperature, the crystal undergoes a phase transition which is also called displacement phase transition [29, 30]. Therefore, the crystal structure of BaTiO₃ is also temperature and stress dependent, as shown in Figure 3. Above the Curie temperature Tc, ~133°C, depending on the impurity content [31], the cubic structure ***Pm3m*** is stable with a=4.009 Å [32]. When cooling through the Curie temperature between 130°C and 0°C, the tetragonal structure (***P4mm***, a=3.992 Å, c=4.035 Å) is formed with octahedron distortion and positive ion shifting off the center position, as shown in Figure 3(a) [32]. Associated with this distortion is a displacement of the titanium and oxygen atoms, as shown in Figure 3(b).The formation of the tetragonal structure makes the unit cells turn out to be permanently polarized, which leads to spontaneous polarization along the c-axis [3, 33]. Since there are six equivalent <100> axes in the cubic phase, upon cooling the polarization can arise parallel to any one of these six equivalent directions. It is the ability to reorient the spontaneous polarization with an external electric field that makes this ferroelectric material so interesting to study. Figure 4 shows the distortion of the BaTiO₃ unit cell with temperature over a sequence of transitions [34]. The temperature of the phase transitions could be shifted a little because of the purity of barium titanate. As shown in Figure 4, upon further cooling below 0°C, the unit cell distorts again and the tetragonal structure changes to orthorhombic structure by elongating along the face-diagonal direction [35]. There are 12 equivalent <110>

directions in the original cubic phase, which results in 12 possible polar directions in the orthorhombic phase.
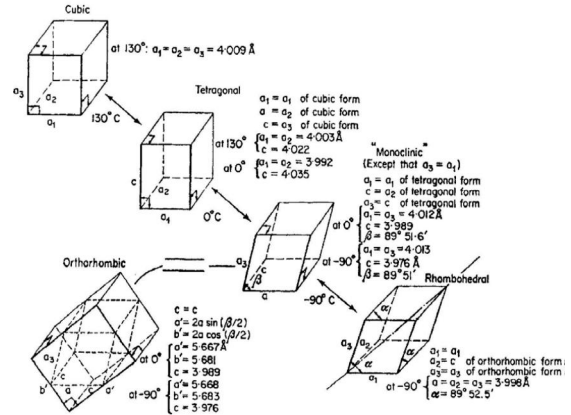

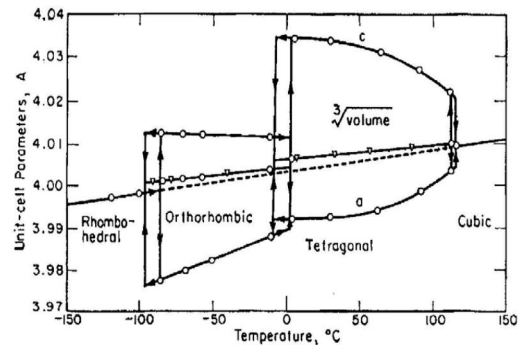Figure 4 Distortion of BaTiO₃ unit cell showing temperature dependence.

Figure 5 Lattice constants of BaTiO₃ as a function of temperature.

This phase is stable from approximately 0~5°C to -90°C. Below -90°C, the unit cell undergoes another distortion along the body diagonal, resulting in a rhombohedral (R3m) symmetry. There are 8 equivalent polar directions along the original cubic <111> direction in this phase. Figure 5 shows the variation of BaTiO₃ lattice parameters at different cooling temperatures. Three phase transition ranges are clearly seen in the figure. The exact transition temperatures and amount of distortion are a function of cooling rate, residual stresses, and purity of the material [36]. The size ratio of the c-axis to a-axis for pure BaTiO₃ is approximately 1.01 at room temperature, and therefore, the spontaneous strain for BaTiO₃ is approximately 1% at room temperature.

Conclusion

In this work we have discussed about the pervoskite nature of BaTiO₃ . The phase transition and Crystal structure also been studied. We concluded that

this material will show the ferroelectricity behavior. In future we will discuss about the ferroelectric behavior of $BaTiO_3$

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