GRAIN CORE-GRAIN SHELL STRUCTURE AND LATTICE DEFECT IN SrTiO$_3$ CERAMICS

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ABSTRACT

The core-shell structure in SrTiO$_3$ grains has been discovered with the analytical electronic microscope (AEM). Further studies show that the core-shell structure is formed due to the inhomogeneous distribution of Pb and Bi ions, which may influence the physical properties of ceramics. Additionally, high-resolution lattice images reveal the partial edge-sharing of octahedra in the SrTiO$_3$ crystal lattice, and this kind of lattice defect is not common in the structure of the ABO$_3$-type ceramics.

Keyword: grain core, grain shell, lattice defect, ceramic.

I. INTRODUCTION

Since Kahn's report[1] of the grain core-grain shell structure in BaTiO$_3$ ceramics, researchers have paid great attention to the study of how this core-shell structure is related to crystal lattices, atomic compositions and physical properties[2-4]. However, there have still not been any reports about whether the core-shell structure exists in other ceramics than BaTiO$_3$ and how, if any, they affect physical properties of ceramics. In this paper, we will present our work on this aspect: We have first observed the core-shell structure in SrTiO$_3$ ceramics with AEM and investigated lattice structures and compositions in the core-shell region and the relation between the core-shell structure and ceramic physical properties. Furthermore, we have studied the structure defect of SrTiO$_3$ in the atomic scale with a high-resolution electron microscope (HREM) and discovered that this defect is related to the arrangement of the oxygen octahedra in the structure. The lattice image and its crystal structure model reveal the existence of edge-sharing arrangement of the oxygen octahedra in SrTiO$_3$, and this kind of lattice defects is not common in the structure of the ABO$_3$-type ceramics.

Raw materials used were TiO$_2$ and SrCO$_3$, and a small amount of PbO and Bi$_2$O$_3$ was mixd in them to modify the properties. Ceramic samples were prepared in the process of ball-milling, prefiring, grinding, dry pressing and sintering and cut to small disks of 3 mm in diameter and 25 μm in thickness. Then, they were thinned by an Argon ion beam till a hole formed in the center. The fringe thickness of the hole was about several hundreds Å, which was suitable for electron microscope (EM)

observation. For all the observations we used JEM-200CX AEM and HREM.

II. CORE-SHELL STRUCTURE IN SrTiO₃

Lots of EM observations revealed the existence of core-shell structure frequently in SrTiO₃ ceramic grains, especially in grains of about 4 μm in size. Fig. 1 shows the grain core-grain shell structure in SrTiO₃ ceramics. From the figure we can see that the core (marked by C), about 1 μm in size, is inlaid in the grain and surrounded by the grain shell (marked by S). In the following, we shall respectively discuss the core-shell structure, composition and its relation with ceramic properties.

1. *Lattice Structure of Core-Shell*

The structure of SrTiO₃ is of the ABO₃-type perovskite, its lattice parameter being 3.905 Å. Selective electron diffraction was used in the observation, and micro-region structure analysis was performed to grains in the core-shell structure. On the right part of Fig. 1, C and S respectively denote the selective electron diffraction patterns of grain cores and grain shells, which were found, by indexing the diffraction patterns, to be of the SrTiO₃ structure. (100), (010) and (110) crystal planes with low indices appeared due to the incident electron beam in the [100] direction.
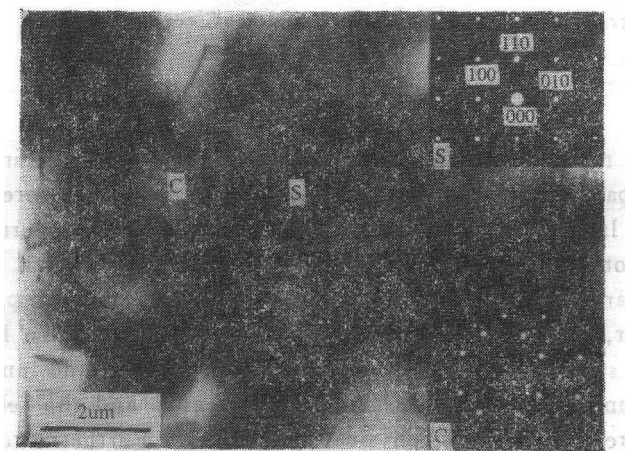

Fig. 1. TEM photograph of the grain core-grain shell structure in SrTiO₃ ceramics.
S, The grain shell; C the core. The right part is the result of corresponding
selective electron diffraction pattern.

Fig. 2 is the grain-shell's lattice image projected in the [100] direction. The lattice fringes of (100) and (010) perpendicular to each other can be seen clearly in the lattice image, and bisecting them is the (110) lattice with $d = 2.8$ Å in regular arrangement. The grain cores are so thick that their lattice image cannot be directly obtained. However, the diffraction patterns in Fig. 1 confirm that there is no difference between spacing and relative positions in lattices of the core and shell regions. Therefore, the lattice structures in the core and shell regions of SrTiO₃ ceramics remain unchanged. However, difference in the intensity of diffraction spots may be found if we observe carefully the diffraction pattern of the core-

shell region in Fig. 1. To explain this difference, we use the following structure factor equation which manifests weight factors for diffraction spots.

$$F_{hkl} = \sum_{1}^{n} f_i \exp[2\pi i(hx_i + ky_i + lz_i)],$$

where f_i are atomic scattering factors, different from each other for different kinds of atoms, (hkl) is the index of the crystal plane and x_i, y_i, z_i are respective spacial positions of atoms. Being of the ABO₃-type perovskite structure, the unit cell of SrTiO₃ is composed of one Sr atom, one Ti atom and three O atoms. Using their atomic spacial positions, we get the following results.

$$\begin{cases} F_{100} = f_{Sr} - f_{Ti} - f_{O_1} - f_{O_2} + f_{O_3}, & \text{if } h + k + l = \text{odd number}, \\ F_{110} = f_{Sr} + f_{Ti} + f_{O_1} - f_{O_2} - f_{O_3}, & \text{if } h + k + l = \text{even number}. \end{cases} \quad (1)$$
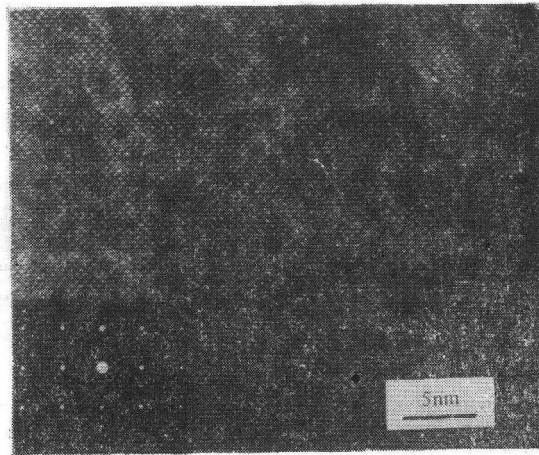

Fig. 2. [001] lattice image photograph of the SrTiO₃ grain shell (the lower left part is its selective electron diffraction pattern).

It can be seen from Eq. (1) that F_{110} is larger than F_{100} by a factor of 2 f_{Ti}, and therefore, the intensity of (100) or (010) diffraction spot is weaker than that of (110) spot, which is in correspondence with the diffraction pattern of the shell region in Fig. 1. Nevertheless, it can be seen from the above relation that doping Pb and Bi atoms in grains may influence the diffraction pattern if the distribution of doped atoms is inhomogeneous. Therefore, it is necessary to further the investigation of the formation mechanism of the core-shell structure from the distribution of atom composition.

2. Atomic Composition in Core-Shell

In an SrTiO₃ grain, if atoms (including Pb, Bi dopants) are distributed homogeneously in respective lattice positions, the diffraction pattern has the features in the shell region shown in Fig. 1; if there is a distribution deviation of atoms in the lattice, the electron beam's scattering intensity in different crystal planes will change correspondingly. Fig. 3 shows the result of analysis on atomic compositions in the SrTiO₃ grain core-grain shell by the X-ray energy disperse spectrum. The energy

spectra of the core and shell verify that the core-shell structure in $SrTiO_3$ grains is formed mainly due to the distribution inhomogeneity of Pb and Bi atoms. In the spectrum of the grain shell of Fig. 3(a) the spectrum peak of Pb is relatively weaker than that of Ti and Sr, while that of Bi is much weaker. However, in the spectrum of the grain core of Fig. 3(b), the peaks of Pb and Bi in the core region are much stronger than in the shell region of Fig. 3(a). It therefore confirms that the formation of the core-shell structure is mainly due to the inhomogeneous distribution of Pb and Bi atoms in grains. As Pb and Bi have much greater atomic numbers than Sr and Ti, their atomic scattering factors are correspondingly larger. When Sr and Ti atoms are substituted by Pb and Bi respectively, the former lattice diffraction intensity may change, which results in the electron diffraction pattern of the core region shown in Fig. 1.
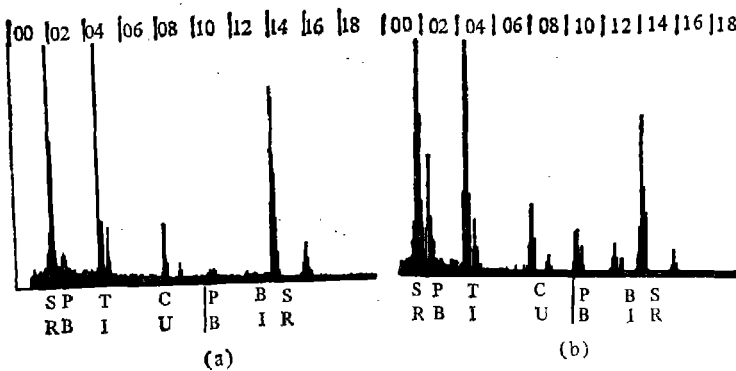
Fig. 3. Result of EDS of $SrTiO_3$ grain shell (a) and that of EDS of $SrTiO_3$ grain core (b).

3. Relation of Core-Shell Structure and Its Physical Properties With Preparing Technology

After the confirmation of the formation mechanism of the core-shell structure in $SrTiO_3$ grains, it is undoubtedly necessary to further investigate how the core-shell structure is related to the physical properties and preparing technology of $SrTiO_3$ ceramics. Hence we focus our study on two special high-voltage ceramic capacitor

Table 1

The Relationship Between Properties and Content of Pb, Bi in $SrTiO_3$ Grain Core-Grain Shell

Analyse Item	Grain Shell		Grain Core		Insulation Intensity	Resistivity	Dielectric	Dielectric
Samples	Pb	Bi	Pb	Bi	(kV/mm)	($\Omega \cdot cm$)	Constant	Loss
Sample I (box-type)	10.85	10.17	3.44	3.10	8	10^{11}	2500	<0.01
Sample II (kiln-type)	0.51	0.51	7.74	3.66	4	10^{11}	2100	<0.02

samples whose physical properties are rather different. There listed in Table 1 are the principal physical properties of the two samples and Pb and Bi compositions in the core and shell regions. Samples I and II were respectively sintered in a box-type and a kiln-type furnace. It is shown in Table 1 that the properties of Sample I prepared in the box-type furnace is much better than that of Sample II prepared in the kiln-type furnace. The Pb and Bi compositions were obtained by EDS. It is very interesting that the Pb and Bi compositions of the two samples are obviously different: the Pb and Bi compositions of Sample I in the shell region are three times as much as that in the core region, but Sample II is opposite to Sample I. It is clear that the difference in properties of the two samples is caused mainly by the distribution difference of Pb and Bi compositions in the core and shell regions. Sample I was sintered in relatively isolated furnace where it was not easy for Pb and Bi atoms to vaporize, while Sample II was sintered in a kiln-type furnace which was much less airtight than the box-type furnace. At high temperature, Pb and Bi atoms can easily vaporize in a kiln-type furnace, and as a result, the Pb and Bi compositions in the shell region are much smaller than that in the core region. In SrTiO₃, the doping of Pb was to adjust the Curie temperature of ferroelectric ceramics and the dielectric constant at the Curie temperature. Bi was used to widen the Curie temperature, to make the dielectric deviation near the Curie temperature smaller, thereby to produce a relatively stable ceramic capacitor, and furthermore to increase the insulation intensity and decrease dielectric loss. Obviously, in a high-voltage ceramic capacitor of SrTiO₃, the larger the region of the grain shell is, the more sensible the ceramics is to high voltage. Nevertheless, the performance will be badly influenced if the vaporization of Pb and Bi atoms in the shell region is great and doping is not effective.

It is shown that the core-shell structure of SrTiO₃ ceramic grains may greatly influence ceramic properties, and the formation of this structure is closely related to the preparing technology. With a proper technological process, we may take advantage of this special core-shell structure to improve the properties of materials. The discovery of the core-shell structure is significant for the study of the relation of microstructures with physical properties and preparing technology.

III. CRYSTAL LATTICE DEFECT IN SrTiO₃

Defects of SrTiO₃, as medium of high-voltage ceramic capacitors, will directly affect its insulation strength. More defects have been found in the core-shell region, which give us an opportunity to further study their structure characteristics. Fig. 4 is the high-resolution lattice image of the SrTiO₃ grain shell along the [111] direction, the upper left part being the corresponding selective diffraction pattern. The lattice image and diffraction show that the SrTiO₃ lattice projected along the [111] direction is arranged in the rhombohedral form. As indicated by P in Fig. 4, the three (110) lattice planes are regularly arranged at an angle of 60°. From the lattice image and electron diffraction we can see that the projection feature of the SrTiO₃ lattice along the [111] direction is actually a result of the arrangement of Ti-O octehedra in the rhombohedral form. The model in Fig. 5(a) illustrates the arrangement of Ti-O octehedra projected along the [111] direction. It is in accordance with the Pauli principle that the oxygen octehedra are corner-linked to form a
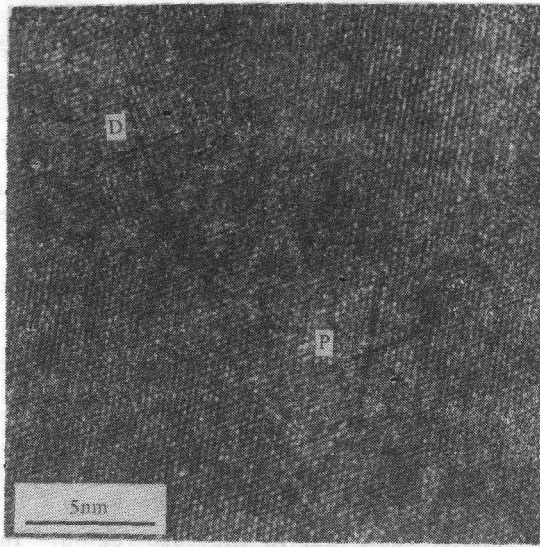
Fig. 4. [111] lattice image of SrTiO₃ grain shell. D, Lattice defect region; P, perfect lattice region.

○ O   ◎ Ti (Sr)

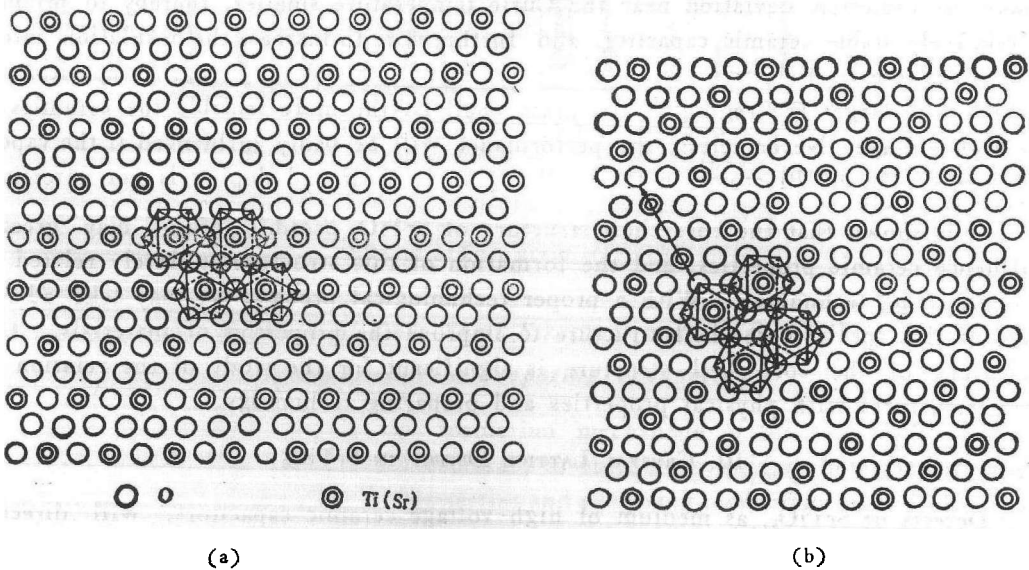(a)   (b)

Fig. 5. Atomic structure model (projected along [111]) of SrTiO₃ crystal lattice and schematic diagram of oxygen octehedra arrangement (a) and that corresponding to the defect region in Fig. 4 and schematic diagram of edge-linked arrangement of oxygen octehedra (b).

stable structure in the ABO₃-type perovskite compound. Therefore, the region marked by P is the perfect crystal lattice of SrTiO₃. Nevertheless, after careful observation at the region marked by D in Fig. 4, we have found that the horizontal fringe (marked by a black cross) is of the same period as that of P region, and the other two periodic arrangements at an angle of 60° are substituted by a set of vertical lattice fringe, which results in a perpendicularly arranged abnormal lattice region. From the perfect lattice structure of Fig. 4 and related structure model of Fig. 5(a) we deduce

that the abnormal lattice region D of Fig. 4 is induced by the slip of some atoms along the (110) plane which in turn changes the lattice of the two (110) crystal planes inclined at the angle 60°. Obviously, the abnormal lattice arrangement in region D indicates that the arrangement of the octehedra in $SrTiO_3$ has also changed. Nevertheless, in previous three sets of (110) lattice fringes at an angle of 60° there is still a set of fringe that has a regular period, the same as that in region P; that is, in one direction the oxygen octehedra are arranged in the way of corner-sharing. Fig. 5(b) is a corresponding structure model constructed according to the structure characteristics of abnormal region D in Fig. 4. From the lattice defect model of Fig. 5(b) we can see that the oxygen octehedra are arranged tetragonally and have the corner-linked (110) lattice period in the direction indicated by the arrow, of which the consequence is the appearance of the abnormal lattice structure in region D in Fig. 4. It is also known from Fig. 4 (region D) and Fig. 5(b) that in $SrTiO_3$ structure, some of oxygen octehedra are connected tetragonally rather than rhombohedrally. This kind of connection cannot be realized unless the octehedra are arranged in the way of edge-sharing. According to the Pauli principle, the edge-lined structure is not as stable as the corner-lined structure. Therefore, this kind of lattice defects is possibly caused by the immigration of Pb and Bi atoms in the sample preparing process.

IV. Conclusions

1. The core-shell structure exists in $SrTiO_3$ ceramic grains, which is formed by the inhomogeneous distribution of Pb and Bi atoms.

2. The grain core-grain shell structure has some connections with preparing technology and physical properties of materials and is significant in materials science.

3. There are plenty of defects in the $SrTiO_3$ grain core-grain shell, including the lattice defect of edge-sharing of oxygen octehedra.

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