

DETERMINATION OF THE ELECTRON DENSITY DISTRIBUTION IN TETRAGONAL BaTiO₃ USING THE MAXIMUM ENTROPY METHOD

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ABSTRACT

Synchrotron radiation and the maximum entropy method (MEM) were used to study the nature of chemical bonding in tetragonal BaTiO₃, and the results were compared to those of cubic SrTiO₃. The MEM charge-density map revealed that Ba is essentially ionic, while Ti-O bond is covalent. A difference in the charge-density distributions of Ti-O bonds in BaTiO₃ and SrTiO₃ is detected, even though the Ti-O bonds in these compounds are essentially covalent in nature. The covalency of the Ti-O bond is, however, weaker in BaTiO₃ than in SrTiO₃. This suggests that BaTiO₃ is more ionic. The difference in structure phase transitions between BaTiO₃ and SrTiO₃ can be attributed to the variations in the nature of the Ti-O bonds in these two compounds.

INTRODUCTION

BaTiO₃ is a ferroelectric compound. There are many studies concerning its crystal structure, phase transition, electric and other properties. The reason for a ferroelectric phase transition (due to condensation of zone-center optical phonons) which occurs in BaTiO₃ and a different structural phase transition (due to condensation of zone boundary phonons) occurring in SrTiO₃ is not clearly understood. Generally speaking, the differences in behavior of these two compounds have been attributed to differences in lattice dynamics, i.e. force constants between constituent atoms. Since force constants are related to the nature of chemical bonding in a material, it is expected that the chemical bondings in BaTiO₃ and SrTiO₃ are significantly different from each other.

In this study, we chose to use the MEM method to study the nature of the chemical bonding in tetragonal BaTiO₃ and to see if we could find crystal-structure evidence which would provide us with an explanation for the differences in the phase transitions occurred in BaTiO₃ and SrTiO₃.

EXPERIMENTAL

Accurate integrated X-ray diffraction intensities are essential if one wants to obtain reliable information on chemical bonding states. We selected the powder diffraction

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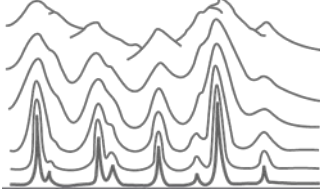
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method because it has the advantage of being able to eliminate multi-domain problems and exclude extinction effects.

The sample we used was a 99.95% pure BaTiO₃ powder. Synchrotron radiation and an imaging plate (IP) detector were used to obtain good counting statistics as well as high angular resolution (peak width at half maximum intensity of 0.03 degrees of 2 theta) from a large Debye-Scherrer camera installed at BL02B2, Spring-8.

A precipitation method was used to produce a specimen consisting of small particles which would produce a diffraction pattern with rings (reflections) that have a homogeneous distribution of intensity along the entire circumference of the rings. Details of the equipment are described in reference [1]. The sample was sealed in a 0.2-mm diameter quartz capillary. The wavelength of synchrotron radiation used in this study was 0.5 Angstrom to measure over an angular range up to 80 degrees of 2 theta.

MEM/RIETVELD ANALYSIS

A MEM/Rietveld analysis was used to calculate the charge-density distribution in tetragonal BaTiO₃. Details of the method are given in references [2-5]. A preliminary Rietveld analysis was done to obtain crystal-structure parameters. Results are listed in Table 1, and fitting results are plotted in Figure 1. An R-factor (an expression of reliability) of 3.9% was obtained from the intensities of the measured Bragg reflections. The results were in excellent agreement with those obtained in an earlier single-crystal analysis [6]. The experimental structure factors were measured by using intensities from individual reflections. 331 structure factors were measured. A MEM calculation was then used with these 331 structure factors, and the unit cell was divided into 144 x 144 x 144 pixels for high resolution.

Table 1

Space Group:P4mm
a=3.09914(1) Å, c=4.0335(1) Å

	x	y	z	B(Å ²)
Ba	0.0000	0.000	0.000	0.331(4)
Ti	0.500	0.500	0.488(1)	0.51(2)
O ₁	0.500	0.500	0.007(9)	0.59(7)
O ₂	0.500	0.000	0.515(3)	0.51(3)

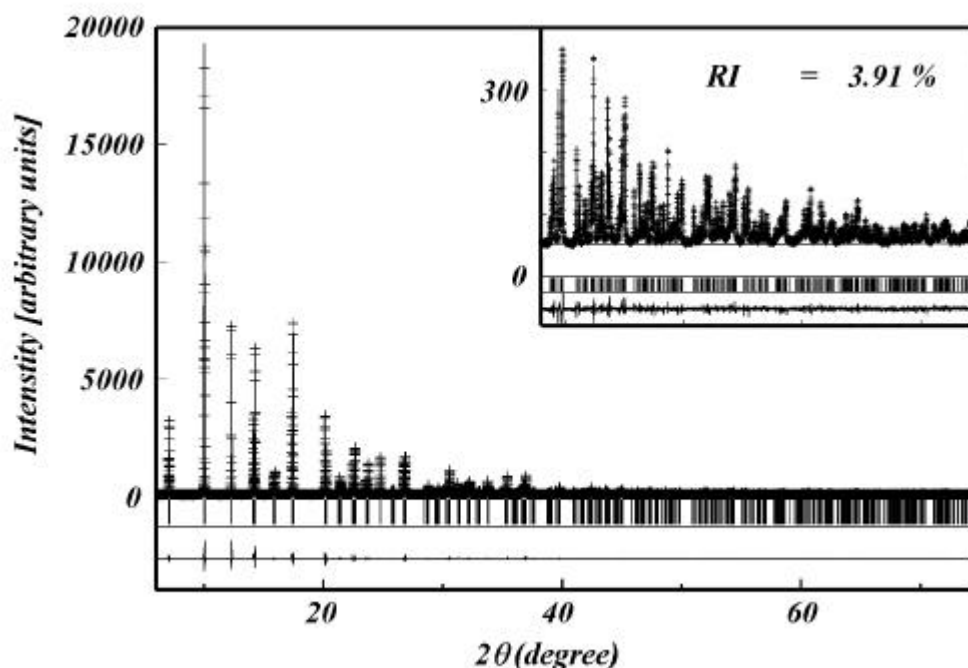


Fig. 1

MEM CHARGE-DENSITY MAP OF TETRAGONAL BaTiO₃

Figure 2 shows the MEM charge-density map of tetragonal BaTiO₃ on the (110) plane. From the MEM charge distributions, it appears that Ba is essentially ionic and the Ti-O bond is covalent. There may be very weak covalency between Ba and O ions. The significance of such weak covalency (if it exists) is not made clear by this study. We are currently performing additional studies of other perovskite compounds.

Due to the slight displacements of Ti and O ions opposite to each other along the [001] direction in tetragonal BaTiO₃, two Ti-O bonds on this plane are not identical, i.e. the Ti-O bond is slightly shorter than the O-Ti bond. The small difference is reproducible in the MEM charge-density distribution and can be seen from the charge-density distributions between Ti-O and O-Ti bonds, which shows a small displacement of Ti ions in BaTiO₃. It may conclude from the density map that a chain of Ti-O-Ti-O-Ti-O-Ti... along the [001] direction in the tetragonal BaTiO₃ is paired with Ti-O, Ti-O and so on.

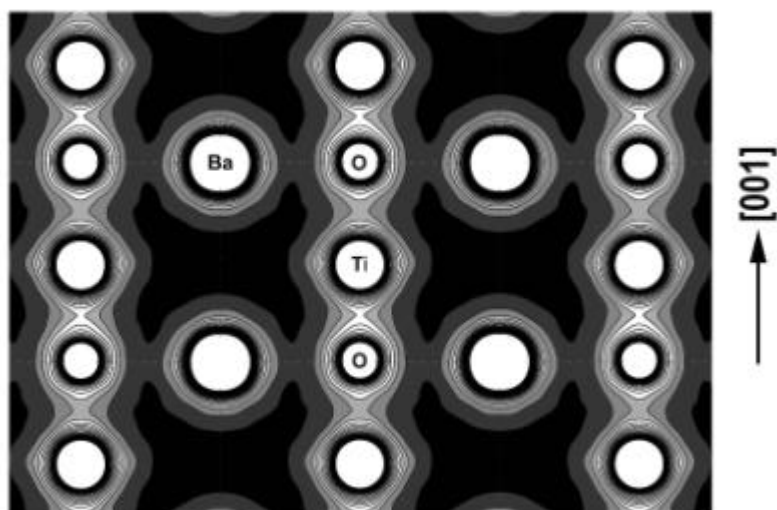


Fig.2

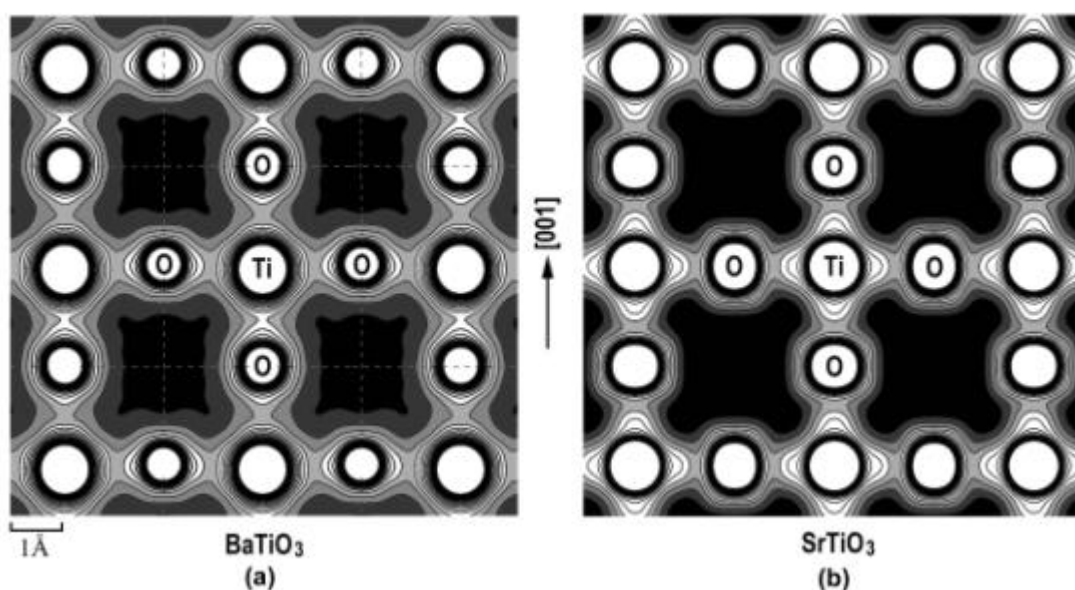


Fig. 3

In order to discuss the difference in the covalency between the Ti and O atoms in perovskite oxide crystals, the charge-density distribution of BaTiO₃ was compared with that of SrTiO₃. In Fig. 3 the MEM charge-density distribution on the (200) plane, perpendicular to the (001) plane, of BaTiO₃ is compared with that of SrTiO₃ [7]. It can be seen from Fig. 3 that BaTiO₃ has a tetragonal symmetry, while SrTiO₃ has a cubic symmetry. The Ti-O bond is significantly stronger in SrTiO₃ than in BaTiO₃. This can be explained by the difference in the packing of atoms in their unit cells; the lattice constant $a = 3.904 \text{ \AA}$ of SrTiO₃ is shorter than that of

BaTiO₃ with $a = 3.989 \text{ \AA}$ and $c = 4.029 \text{ \AA}$. It is well known that the longer the bond length, the weaker the covalent bond. Therefore, the covalency of Ti-O bonding in BaTiO₃ is weaker than that of SrTiO₃. In other words, BaTiO₃ is more ionic in nature.

It is well known that there is a soft phonon mode Γ_{15} at the Brillouin zone center for both BaTiO₃ and SrTiO₃, and only BaTiO₃ has a phase transition at 120 K as a consequence of the instability of such a soft phonon mode, while SrTiO₃ does not. SrTiO₃, instead, has a structural phase transition at -168 °C, because of the condensation of the zone-boundary phonon R_{25} , which is hindered the oscillation motion of oxygen octahedron around a Ti ion. Hence, the displacement of oxygen through the phase transition is not the same. The different nature of the two phase transitions can be explained by considering the difference in the degrees of covalency or ionicity between BaTiO₃ and SrTiO₃. The oxygen octahedron around a Ti atom can be easily be distorted in BaTiO₃ because of its ionic nature. Furthermore the charge-density distributions around Ti and O atoms are distorted and asymmetric with respect to the plane perpendicular to the [001] direction. This indicates that these ions are polarized and responsible for the ferroelectricity of BaTiO₃.

It should be noted that there is a significant difference in charge densities around Ti atoms between BaTiO₃ and SrTiO₃. This difference has not been reported previously, and it reflects the difference in bonding nature, consequently the difference in the degree of covalency and ionicity.

CONCLUSION

A detailed experimental charge-density distribution has been determined for tetragonal BaTiO₃. It reveals the nature of chemical bond of this compound. Ba is found to be almost ionic, while the Ti-O bond is essentially covalent. A significant difference in the MEM charge-density distributions between BaTiO₃ and SrTiO₃ has been detected. This indicates ionic character in the covalent bond between Ti and O atoms in BaTiO₃. It suggests also that the different nature in the phase transitions in BaTiO₃ and SrTiO₃ is due to a slight difference in the covalency of the Ti-O bonds in these two compounds.

The above comparison was based on the charge-density distributions of tetragonal BaTiO₃ and cubic SrTiO₃ obtained from room-temperature experiments. It is hoped that an understanding of the charge densities of typical perovskite compounds with different types of structural phase transitions, such as KMnF₃, CsPbCl₃, PbTiO₃, etc. can be obtained in a comprehensive MEM study now in progress.

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