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Structure of BaTiO₃*

EDWARD G. GRIMSAL

The theoretical model for the ferroelectric effect in barium titanate (Mason and Matthias, 1948) assumes a displacement of the titanium from the center of the unit cell in the *z* direction, probably due to the formation of a covalent bond with the *c*-centered oxygen. This displacement had been observed earlier by Dr. Danielson (Danielson, Matthias, and Richardson, 1948) and given as about 0.16Å, at 20°C. This value, based on the relatively high intensity of x-ray scattering from the 0-0-11 plane, as shown by a Weissenberg pattern using molybdenum radiation was later brought into question by work at the Institute for Atomic Research (Danielson and Rundle, 1949), using silver radiation. From the Weissenberg pictures obtained at that time, it appeared that the

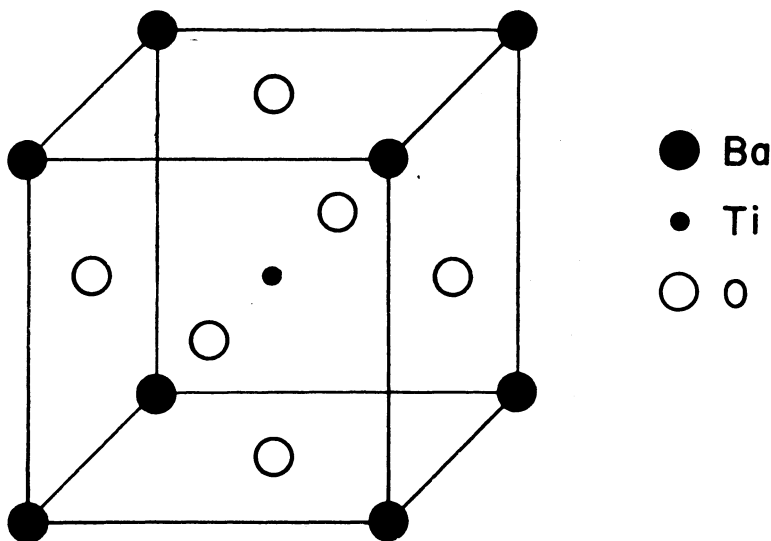
**UNIT CELL FOR BaTiO₃**

Figure 1. Barium titanate is teragonal below 120° C., passing over onto cubic above this temperature. At room temperature the unit cell dimensions are: $a = 3.9946 \text{ \AA}$, $c = 4.0335 \text{ \AA}$.

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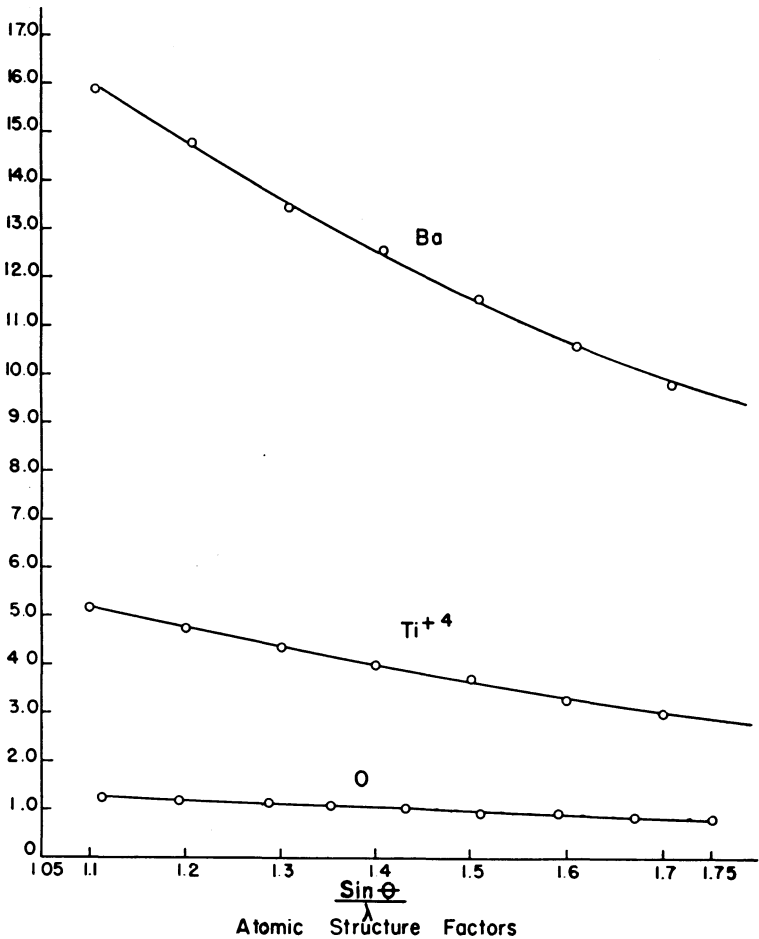


Figure 2. This shows the variation of the atomic scattering factors with $\frac{\sin \Theta}{\lambda}$. The curve for Barium is calculated from the Thomas-Fermi model, while those for titanium and oxygen are computed by interpolation methods.

displacement was less than 0.1A. More recent papers (Kay, 1949; Jaynes and Wigner, 1950) have questioned the fact that this displacement really exists.

In continuing the work of Danielson and Rundle, several refinements have been introduced. Instead of just one picture, a series of pictures were taken using a graduated set of exposure times. From these it was possible to judge the intensity ratios for various sets of reflections to within an estimated accuracy of ten per cent.

Furthermore, the expression for the intensity of the beam reflected from the (hkl) plane was investigated more carefully. This is usually given as,

$$I \propto \frac{1 + \cos^2 2\theta}{\sin 2\theta} e^{-B\left(\frac{\sin \theta}{\lambda}\right)^2} |F|^2 \quad (1)$$

$$F = \sum f_n e^{2\pi i(hu_n + kv_n + \ell w_n)} \quad (2)$$

where θ and λ are Bragg angle and wave length respectively. The first factor $\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right)$ is called the Lorentz-polarization factor and takes into account the polarization of the reflected beam and the amount of time a plane is in a position to reflect. The exponential factor is called the temperature factor and corrects for the thermal vibrations of the atoms. F , the structure factor, depends on the atomic scattering factor, f_n , i.e. the scattering power of the atom, and the position of the atoms in the unit cell (u , v , w). It was found that neither the atomic scattering factors or their ratios remained constant as assumed before. The actual variation of this factor for the various atoms of interest is shown in figure 2.

Using formula (1), we then calculate the values of $|F|^2$ as determined from the intensity ratios. Various values of titanium displacements are substituted into the formula (2) for the structure factors until the best fit, with respect to the values from equation (1), is obtained. It was found necessary to assume that the oxygens were displaced also. The displacement of the c-centered oxygen will hereafter be called Z_2 , that of the a- and b-centered oxygens Z_3 ; while the titanium displacement will be Z_1 . The structure factors for the planes of interest will then be,

$$10\ell, \ell \text{ even} \quad F = f_{Ba} + f_{Ti}e^{2\pi i\ell Z_1} - f_Oe^{2\pi i\ell Z_2}$$

$$10\ell, \ell \text{ odd} \quad F = f_{Ba} - f_{Ti}e^{2\pi i\ell Z_1} - f_Oe^{2\pi i\ell Z_2}$$

$$00\ell, \ell \text{ even} \quad F = f_{Ba} + f_{Ti}e^{2\pi i\ell Z_1} + f_Oe^{2\pi i\ell Z_2} + 2f_Oe^{2\pi i\ell Z_3}$$

$$00\ell, \ell \text{ odd} \quad F = f_{Ba} - f_{Ti}e^{2\pi i\ell Z_1} + f_Oe^{2\pi i\ell Z_2} - 2f_Oe^{2\pi i\ell Z_3}$$

$$11\ell, \ell \text{ even} \quad F = f_{Ba} + f_{Ti}e^{2\pi i\ell Z_1} + f_Oe^{2\pi i\ell Z_2} - 2f_Oe^{2\pi i\ell Z_3}$$

$$11\ell, \ell \text{ odd} \quad F = f_{Ba} - f_{Ti}e^{2\pi i\ell Z_1} + f_Oe^{2\pi i\ell Z_2} + 2f_Oe^{2\pi i\ell Z_3}$$

Two sets of pictures were taken, the crystal being rotated about the a and the $a + b$ axis respectively. From the first set we obtained the following data on the 10l reflections.

Table 1
Observed Intensities

Plane	Rundle	Danielson	Grimsal	Average	After Lorentz-Polarization Correction	After Temperature Correction B = 1.0
(1, 0, 9)	225	220	200	215	203	715
(1, 0, 10)	55	52	60	56	56	264
(1, 0, 11)	100	96	100	99	95	621
(1, 0, 12)	25	26	30	27	22	200
(1, 0, 13)	50	52	50	51	28	372
(1, 0, 14)	30	40		35	8.9	185

From an examination of the structure factors for these planes we see that the intensity ratios are quite sensitive to the titanium displacement Z_1 and very insensitive to any displacement of the oxygen, particularly when we consider the low value of the oxygen atom factor in this region. Table 2 shows the absolute squares of the structure factors for several values of Z_1 and Z_2 , normalized for easier comparison. The last column in this table shows the calculated range of the observed $|F|^2$. In all cases the range is $\pm 10\%$ except for the 1-0-14 value which is $\pm 15\%$, as observed. Thus we see that there is a definite displacement of $(.011 \pm .003)c$ or $.045 \text{ \AA} \pm .015 \text{ \AA}$, since $c = 4.03 \text{ \AA}$.

The next step was to see if we could find the oxygen displace-

Table 2
Calculated Structure Factors
From Equation (2)

Plane	$Z_1 = .008$			$Z_1 = .011$			$Z_1 = .014$			Observed from equation (1)
	$Z_2 = .025$.000	-.025	.025	.000	-.025	.025	.000	-.025	
(1, 0, 9)	930	1220	1020	840	975	860	835	895	850	640 — 790
(1, 0, 10)	269	290	258	284	276	250	348	305	292	240 — 290
(1, 0, 11)	635	797	700	560	626	578	560	560	560	560 — 680
(1, 0, 12)	206	210	200	223	207	198	279	236	237	180 — 220
(1, 0, 13)	427	510	468	370	392	380	360	342	362	335 — 410
(1, 0, 14)	160	160	160	175	160	160	220	185	193	160 — 210

ments. The ratio of the structure factors of the (0, 0, 1) and (1, 1, 1) reflection is seen to be very sensitive to Z_3 . There is no such sensitive test for Z_2 , but from the size of the unit cell and the Goldschmidt radius of the oxygen, it seems safe to assume that Z_2 and Z_3 are of the same order.

The data for these comparisons was taken from the set of pictures rotated about the $a + b$ axis, and is shown in Table 3, along with some calculated structure factors.

Table 3

Intensities and Structure Factors For (0, 0, 1) and (1, 1, 1) Reflections

	Average Observed	After Lorentz and Temp- perature Correction	$Z_3 = .015$	$Z_3 = .018$	$Z_3 = -.015$	$Z_3 = -.018$
(0, 0, 9)	45	147	138	143	126	128
(1, 1, 9)	69	233	201	186	236	227
(0, 0, 10)	83	386	421	404	386	365
(1, 1, 10)	70	336	285	291	297	304
(0, 0, 11)	28	174	108	112	97	100
(1, 1, 11)	35	218	135	122	168	158
(0, 0, 12)	41	302	271	246	231	213
(1, 1, 12)	34	255	184	189	194	200
(0, 0, 13)	23	176	84	88	75	79
(1, 1, 13)	33	181	94	82	121	111
(0, 0, 14)	31	150	160	147	137	122
(1, 1, 14)	31	150	120	125	128	132

The agreement in the oxygen calculations is not as good as in the titanium calculations. The results, however, do show that there is an oxygen displacement of the order of $.015c$ to $.018c$, which was not postulated previously. The lack of complete agreement in the oxygen displacement calculations could be the result of one or both of the following: Excessive absorption of the x-ray beam by the crystal, or the crystal may have exceeded the allowable size for the Lorentz-polarization factor we have used.

Either of these would lower the reflected intensity in the higher orders, giving the above diverging results. Further measurements, on a smaller crystal, are now being made with the hope of achieving better agreement in the oxygen displacement calculations.

Thus it appears that there is a displacement of both the titanium and the oxygen. The evidence for the titanium displacement is very conclusive and we can give this a definite value of $.045 \pm .015A$. While there is not nearly so convincing an argument for the dis-

placement of the oxygens, I feel it is safe to say that this exists and is of the order of .07A. Whether these are in the same or opposite direction must be left for future consideration, along with a more accurate evaluation of the oxygen displacement.

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