

The Effect of Various Substituents on the Lattice Constants of Tetragonal Barium Titanate

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The lattice constants of barium titanate, containing varying amounts of dissolved titanium dioxide, stannic oxide, or calcium stannate have been measured at room temperature. The latter two substances cause the lattice to become isometric, the equality of a_0 and c_0 occurring at about 9 mole per cent of SnO_2 , and at about 13 mole per cent of CaSnO_3 . Added TiO_2 has no effect within the accuracy of the measurement.

Introduction

As a part of a program which was initiated to study the electrostrictive properties of barium titanate ceramics, we have measured the lattice constants of barium titanate containing varying amounts of several other compounds. It is well known that the ferroelectric and electrostrictive properties of pure barium titanate at ordinary temperatures depend on the fact that it is polar (tetragonal with $c_0/a_0 > 1$) and that a transition to the cubic form occurs at about 120 °C., with attendant loss of polar properties. In the case of pure barium titanate, as the temperature is raised, a_0 increases and c_0 decreases, the two becoming equal at the transition temperature (Megaw, 1947; Kay & Vousden, 1949). As described below, somewhat similar changes at room temperature are caused by the presence of certain added substances.

Experimental

The compositions described below were prepared as ceramic sheets by firing rolled slurries of each at about 1300 °C. for approximately 20 minutes. X-ray diffraction patterns were recorded from a Norelco diffraction unit with a Geiger counter. The samples were rotated during the recording of the pattern. No attempt was made for precise control of the temperature. All measurements, however, were made in an air conditioned laboratory, at an ambient temperature of 24 ± 5 °C. In this range, the temperature coefficients for both lattice constants are less than $0.0001 \text{ \AA degree}^{-1}$ (Megaw, 1947). Values of the Bragg angles of resolved reflections were read directly from the recorded pattern. In the range $\theta = 45^\circ$ to 70° more than ten well resolved maxima could be measured with some confidence, although the resolution was quite sensitive to the axial ratio. In order to simplify the calculations, the values of c_0 , a_0 , and c_0/a_0

were determined from the observed values of θ for the pair of reflections (224) and (422). These two reflections occur at $\theta \sim 70^\circ$. In the cases where (224) α_2 was not resolved from (422) α_1 the observed value of $\sin \theta$ of (422) α_2 was multiplied by the factor 0.99506 to give an effective value for $\sin \theta$ of (422) α_1 .

The reliability of the method of using only the above pair of lines in determining lattice constants was checked by using the θ values for 13 resolved lines observed for c.p. barium titanate powder (not fired) in a least-squares treatment based on the relation:

$$\sin^2 \theta_{hkl} = (h^2 + k^2)\lambda^2/4a_0^2 + (l^2)\lambda^2/4c_0^2 + \delta \sin^2 2\theta_{hkl},$$

where δ is a drift correction (Klug & Alexander, 1954).

The results of the two methods of determining c_0 , a_0 , and c_0/a_0 are compared in Table 1. The agreement suggests

Table 1. *Lattice constants of c.p. BaTiO₃ by different methods*

	By least squares on 13 lines with drift correction	From observed θ for (224) and (422)
a_0	3.993 ₉ Å	3.993 ₈ Å
c_0	4.034 ₆	4.035 ₇
c_0/a_0	1.010 ₂	1.010 ₅

that the simple two-line method for determining lattice constants is accurate to about 1 part in 4000, if the more precise least-squares method is taken as standard. The drift correction for all of the compositions measured would not be expected to differ much from that found for c.p. barium titanate.

Results

1. Variations among commercial lots of BaTiO₃

Lattice constants for six different lots of commercial grade barium titanate were measured first, in order to

determine the magnitudes of the variations among them. The various lots were obtained from Titanium Alloy Division of the National Lead Company; according to analytical data, they differ in containing slight calculated excesses of barium oxide or titanium oxide. The results of the X-ray studies are presented in Table 2.

Table 2. *Lattice constants of commercial grade BaTiO_3*

Lot no.	a_0	c_0	c_0/a_0
37	3.994 ₆ Å	4.031 ₄ Å	1.009 ₂
45	3.994 ₁	4.032 ₄	1.009 ₆
49	3.994 ₇	4.031 ₃	1.009 ₂
66	3.994 ₈	4.032 ₁	1.009 ₃
73	3.995 ₄	4.030 ₂	1.008 ₇
78	3.994 ₇	4.031 ₀	1.009 ₁

The differences found are not significant. As compared with c.p. barium titanate, on the other hand, the values found for a_0 are all about 0.001 Å larger, and the values for c_0 about 0.002 Å smaller.

2. Effect of TiO_2

Ceramics containing up to about 5 mol. % of added titanium dioxide were prepared. Since no trace of any titanium dioxide lines were observed in the first materials, it can be concluded that titanium dioxide dissolves in barium titanate. The results of the X-ray studies are shown in Table 3, where it is seen that the

Table 3. *Effect of TiO_2 on the lattice constants of BaTiO_3*

Mol. % of TiO_2	a_0	c_0	c_0/a_0
0.00*	3.994 ₂ Å	4.031 ₃ Å	1.009 ₂
2.30	3.992 ₇	4.033 ₅	1.010 ₂
3.01	3.993 ₃	4.033 ₂	1.010 ₀
3.70	3.993 ₂	4.033 ₆	1.010 ₁
4.39	3.993 ₂	4.034 ₀	1.010 ₂
4.94	3.993 ₀	4.031 ₈	1.009 ₇

* As found for lot 49, which was used in the preparation of the other compositions.

differences observed are not only small, but of doubtful significance.

3. Effect of SnO_2

As above, in the case of added titanium dioxide, ceramics with added stannic oxide show no trace of

Table 4. *Effect of SnO_2 on the lattice constants of BaTiO_3*

Mol. % of SnO_2	a_0	c_0	c_0/a_0
0.00*	3.994 ₇ Å	4.031 ₃ Å	1.009 ₂
0.99	3.995 ₄	4.031 ₇	1.009 ₁
2.00	3.997 ₈	4.029 ₇	1.008 ₀
2.91	3.999 ₅	4.028 ₀	1.007 ₃
5.61	4.005 ₇	4.024 ₅	1.004 ₇
7.53	4.011 ₃	4.019 ₀	1.001 ₉

* As found for lot 49, which was used in the preparation of the other compositions.

stannic oxide lines. As opposed to titanium dioxide, however, added stannic oxide has a marked effect on the lattice constants of barium titanate, as can be seen from the data presented in Table 4. These data are also shown in Figs. 1 and 2.

Extrapolation of the data of Fig. 2 shows that barium titanate containing about 9.3% stannic oxide would be expected to be isometric at room temperature.

4. Effect of CaSnO_3

Ceramics containing calcium stannate likewise show no trace of calcium stannate lines. In testing the effect

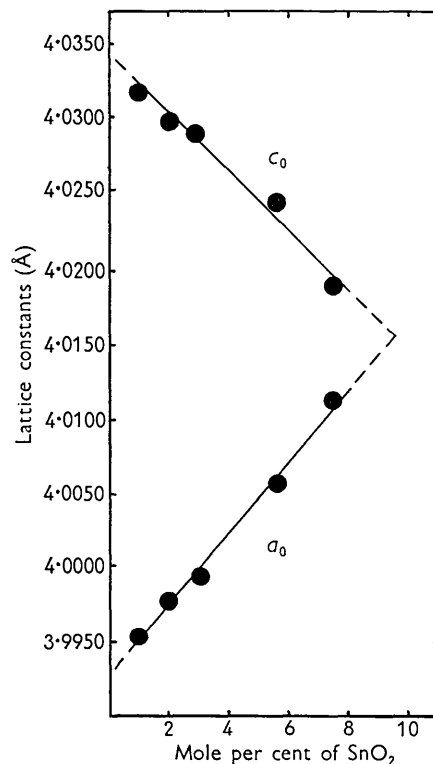


Fig. 1. Effect of SnO_2 on the lattice constants of BaTiO_3 .

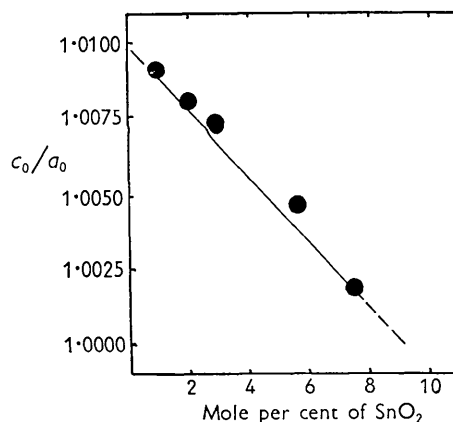
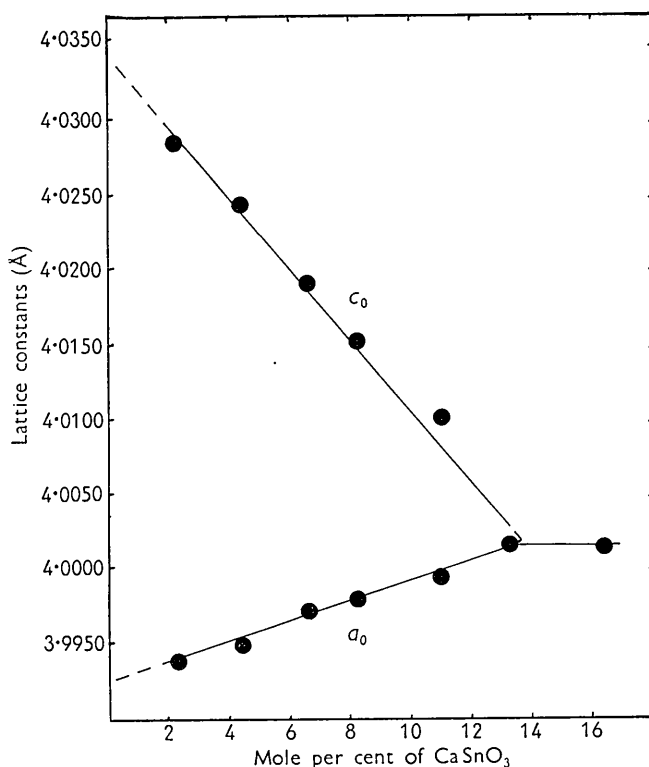
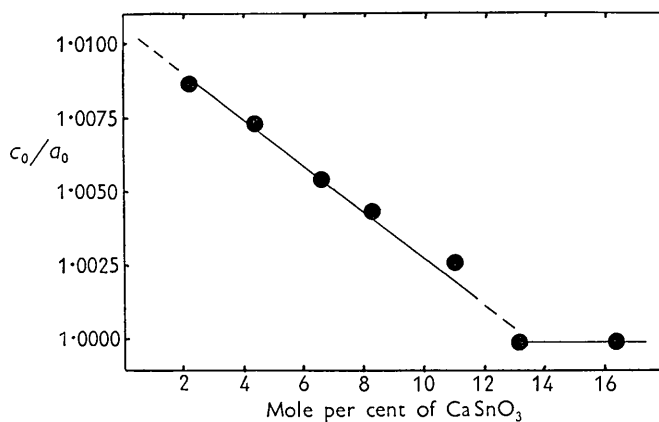


Fig. 2. Variation of c_0/a_0 with SnO_2 content.

Table 5. Effect of CaSnO_3 on the lattice constants of BaTiO_3

Mol. % of CaSnO_3	(Mol. % of TiO_2)	a_0	c_0	c_0/a_0
2.21	2.58	3.994 ₁ Å	4.028 ₈ Å	1.008 ₇
4.41	2.57	3.995 ₂	4.024 ₇	1.007 ₄
6.60	2.56	3.997 ₄	4.019 ₄	1.005 ₅
8.26	2.14	3.998 ₁	4.015 ₆	1.004 ₄
10.98	2.13	3.999 ₅	4.010 ₄	1.002 ₇
13.15	2.13	4.001 ₇	4.001 ₇	1.000 ₀
16.37	2.12	4.001 ₄	4.001 ₄	1.000 ₀


 Fig. 3. Effect of CaSnO_3 on the lattice constants of BaTiO_3 .

 Fig. 4. Variation of c_0/a_0 with CaSnO_3 content.

of calcium stannate, titanium dioxide was added in varying amounts in order to improve the physical properties of the fired material, but since it has already been shown that titanium dioxide alone has no effect on barium titanate, any changes observed may safely be assumed to be due to calcium stannate. The results are presented in Table 5, and in Figs. 3 and 4. As in the case of stannic oxide, added calcium stannate causes a_0 and c_0 to become equal.

Discussion

From the data shown in Figs. 1 to 4, it appears that $\text{BaTiO}_3\text{-SnO}_2$ and $\text{BaTiO}_3\text{-CaSnO}_3$ solid solutions both follow a modified form of Vegard's rule (Vegard, 1921) in that the observed changes in the lattice constants with compositions are linear. It is remarkable that both stannic oxide and calcium stannate have the effect that they do, since neither of them is isomorphous with barium titanate. It is also perhaps somewhat surprising that whereas stannic oxide has a great effect, the similar titanium dioxide has no effect.

Although the reason why pure barium titanate is tetragonal rather than cubic at room temperature is not very well understood, the fact that both stannic oxide and calcium stannate tend to make barium titanate assume a cubic structure should be included in a complete discussion of that phenomenon. The effect cannot be traced in a simple way to the presence of tin, since the axial equality occurs at about 9 mol. % of stannic oxide, as contrasted with the 13 mol. % of calcium stannate required to bring about that condition. It is known that added strontium titanate lowers the transition temperature of barium titanate (Danielson, 1949), and it is therefore surprising that more tin in the presence of calcium ions is required to lower the transition point to room temperature. Furthermore, added stannic oxide causes a_0 to increase more rapidly than it causes c_0 to decrease (Fig. 1); whereas, added calcium stannate has the opposite effect (Fig. 3). Finally, the $\text{BaTiO}_3\text{-SnO}_2$ cubic phase has an extrapolated lattice constant of about 4.005₀ Å, quite a bit larger than the value of 4.001₇ Å obtained for the $\text{BaTiO}_3\text{-CaSnO}_3$ cubic phase, a result consistent with the idea that as calcium ions replace barium ions, the lattice shrinks somewhat. The lattice constant of pure barium titanate at the transition point is 4.009₂ Å (Megaw, 1947).

The results of studies of other properties of some of the above compositions will be described in a later communication.

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