Properties of Barium Titanate in Connection with Its Crystal Structure

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In recent years the uncommon properties of barium titanate ($BaTiO_3$) and some related compounds have attracted much attention. In rapid succession more than 70 publications of various lengths have already appeared, and the subject has been given even more notice since it has become possible to obtain clear crystals from different melts (*4*). In the present paper we will discuss how the abnormal behavior of these dielectric materials is closely related to the structure of the crystal lattice.

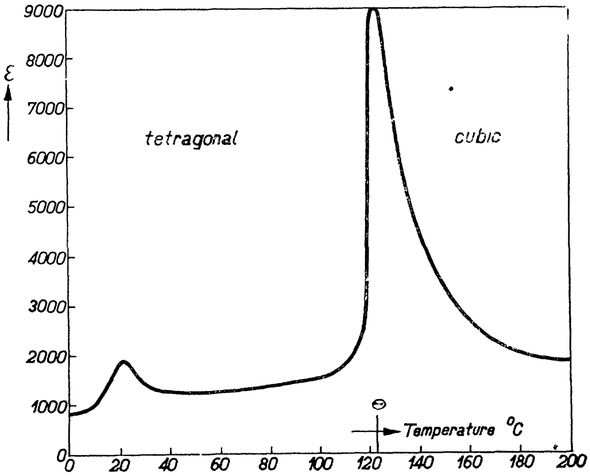

FIG. 1. Dielectric constant of barium titanate measured at low field strengths as a function of temperature.

First we give a general survey of the well-known properties of $BaTiO_3$, the influence of the temperature T and the field strength E on the dielectric constant ε. Fig. 1 shows the relation between ε and T, when measured in a weak a-c field at a frequency between 1 kc and 10 mcps. There is one very high peak in ε at $T = 123°$ C and two small ones at $T = 12°$ C and $T = -70°$ C. The temperature of 123° C (θ) divides this graph into two temperature regions where $BaTiO_3$ shows quite different properties. At temperatures above θ the polarization is a linear function of the electric field strength, the dielectric losses are low, and the only remarkable thing is the steep fall of ε with rising T. The dependence of ε on T in this region is given by a very simple relation:

$$\varepsilon = \frac{A}{T - \theta},$$

A being a constant, approximately equal to the reciprocal value of β, the linear coefficient of thermal expansion.

For $BaTiO_3$ we find experimentally

$$\varepsilon = \frac{102{,}000}{T - 396} \text{ and } \beta = 0.95 \cdot 10^{-5}.$$

In the temperature region below θ the properties are completely changed. ε is no longer a constant, but becomes dependent on the electric field strength. The electric polarization can be considered as composed of two parts: a linear part caused by electronic and ionic displacements, and a nonlinear part which can be saturated at high field strength and which consists of dipole orientation (Fig. 2). The nonlinear part gives only a small contribution to the polarization at low field strengths; at higher field strengths, however, the contribution of this part gradually develops until saturation is reached. The final slope of the hysteresis loop is approximately equal to the initial slope of the initial curve. The dipole contribution causes hysteresis and remanence of polarization, just as in the case of a ferromagnetic material.

The temperature of the peak of ε can be largely influenced by preparing mixed crystals with some other titanates, stannates, and zirconates. Only in the case of mixtures with $PbTiO_3$ do we find an increase of θ, all other additions reducing the value of θ. Solid solutions of these materials are possible, as they all have the same crystal structure, the so-called perovskite structure (perovskite is the mineral $CaTiO_3$). Fig. 3 gives a general picture of the crystal lattice, with a Ti-ion in the center, O-ions at the centers of the faces, and Ba-ions at the corners. In general this is a cubic lattice, but Goldschmidt (*2*) has already shown that there are only few really cubic perovskites. The possibility that three different types of ions will fit in a parameterless cubic structure is not large. Strontium titanate is an example. The unit cell of $BaTiO_3$ shows a slight tetragonal deformation at temperatures up to θ. At this temperature a transition to the cubic form takes place. In the following sections we will discuss the relation between the crystal structure and the electric properties in the different temperature regions.

The high temperature region. Let us consider $BaTiO_3$

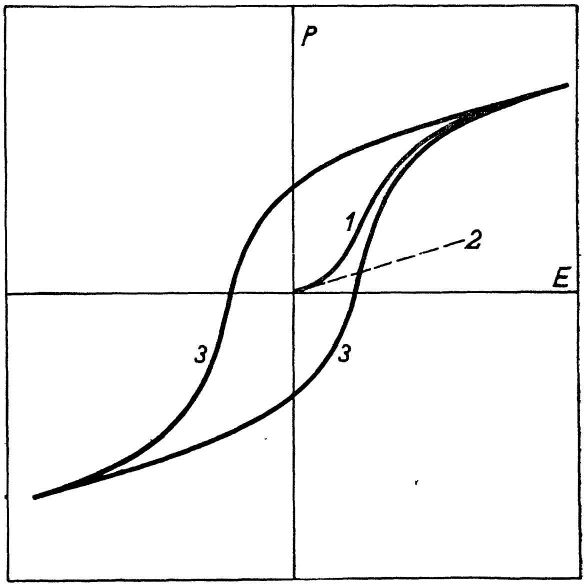

FIG. 2. Electric polarization (P) as a function of field strength (E): 1—initial curve, 2—initial slope of initial curve, and 3—hysteresis loop.

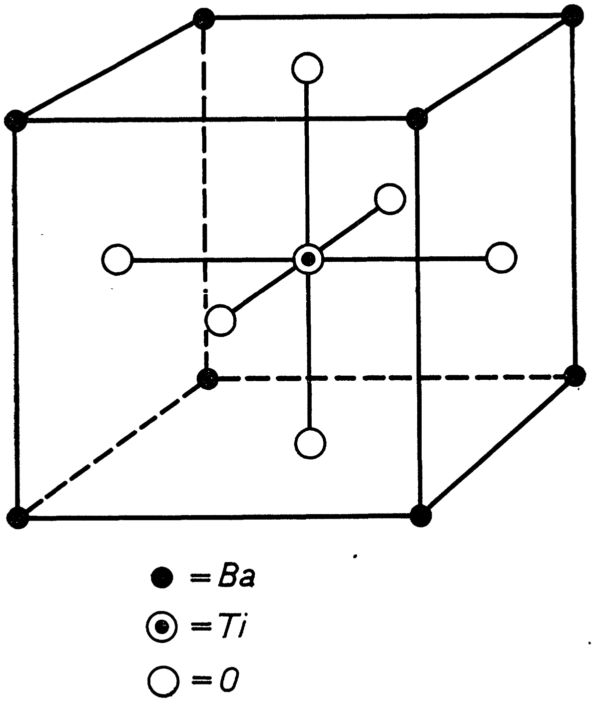

FIG. 3. Unit cell of barium titanate.

above its transition temperature. In this temperature region the substance behaves like a "normal" dielectric, except that the dielectric constant is exceptionally high and strongly dependent on temperature. Before discussing these properties we shall examine more closely the formulas giving the relation between the macroscopic dielectric constant and the properties of the component ions (or atoms).

The well-known formulas of Lorentz-Lorenz and Clausius-Mosotti become for $BaTiO_3$

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} N\alpha^{(e)} = \frac{4\pi}{3} N \left\{ \alpha_{Ba}^{(e)} + \alpha_{Ti}^{(e)} + 3\alpha_{O}^{(e)} \right\} \tag{1}$$

and

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3} N \left\{ \alpha^{(e)} + \alpha^{(i)} \right\}$$
$$= \frac{4\pi}{3} N \left\{ \alpha_{Ba}^{(e)} + \alpha_{Ti}^{(e)} + 3\alpha_{O}^{(e)} + \alpha^{(i)} \right\}. \tag{2}$$

Here n denotes the index of refraction; N is the number of unit cells per cm^3; $\alpha_{Ba}^{(e)}$, $\alpha_{Ti}^{(e)}$, $\alpha_{O}^{(e)}$ are the optical polarizabilities of Ba, Ti and O ions respectively; α^i is the contribution of ionic displacement polarization.

One of the assumptions underlying eqs (1) and (2) is that the environment of every polarizable particle displays cubic symmetry, the local polarizing field then being for each particle:

$$E^{(loc)} = E + \frac{4\pi}{3} P$$

(E = electric field strength, P = polarization).

For crystals for which this symmetry condition is not fulfilled, the Lorentz-Lorenz and Clausius-Mosotti formulas must be corrected and this can be done by adding to the polarizability (*9, 10*) a correction term which depends on the geometrical structure of the lattice and on the polarizabilities of the ions.

In the case of $BaTiO_3$ (see Fig. 3) some ions surround each other in a cubic way while others do not. For example a Ba-ion is surrounded cubically by Ba-ions (its six nearest neighbors are placed at the corners of a regular octahedron) and by Ti-ions (the eight neighbors forming a cube). For oxygen ions, however, the microscopic symmetry is not cubic (its six nearest neighbors are two Ti- and four Ba-ions). Thus for $BaTiO_3$ in eqs (1) and (2), a correction term must be added to the expression between parentheses, but we shall not use it here. In eq (1) the correction proves to be negligible.

When we try to understand the high value of the dielectric constant of $BaTiO_3$ in its cubic temperature region there appear to be at least three contributing factors. First of all $BaTiO_3$ possesses a high refractive index, namely 2.4[5]; thus in eqs (1) and (2): $\frac{4\pi}{3} N\alpha^{(e)} = 0.63$, a rather high value. It is easily seen from eqs (1) and (2) that now a relatively small ionic polarization can give rise to a high dielectric constant. The cause of the high index of refraction is the compactness of the $BaTiO_3$ lattice (the Ba- and O-ions form together a close-packed cubic structure, the Ti-ions being placed in the octahedral interstices) combined with the high optical polarizability of the O- and Ba-ions. In this connection we would remark that in general the optical polarizability of oxygen ions near small, high charge positive ions appears to be much smaller than near large, low charge ions. In the case of oxygen ions next to (tetravalent) Ti-ions, however, this lowering of the polarizability of oxygen does not seem to take place. This high optical polarizability is found in many compounds containing Ti surrounded by six O-ions (TiO_2 in its modifications rutile [$n_\omega(D) = 2.62$, $n_\epsilon(D) = 2.90$], anatase [$n_\omega(D) = 2.56$, $n_\epsilon(D) = 2.49$] and brookite [$n_\alpha(D) = 2.59$, $n_\beta(D) = 2.59$, $n_\gamma(D) = 2.70$]; titanates with perovskite structure [$CaTiO_3$ $n_\epsilon = 2.38$; $BaTiO_3$ $n = 2.4$[5]]; pyrophanite, $MnTiO_3$ showing ilmenite structure [$n_\omega(D) = 2.48$, $n_\epsilon(D) = 2.21$]).

In the second place a high dielectric constant for $BaTiO_3$ is favored by a large contribution from the Ti-ion to the ionic-displacement polarization. Goldschmidt (*2*) has remarked that the perovskite structure ABO_3 would be stable only if the parameter

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

were approximately unity (*6*). This is easily seen from Fig. 3. For $t < 1$ or $t > 1$ the ions A (e.g. Ba) or B (e.g. Ti) respectively have a relatively large space to move in; too large deviations of t from unity give rise to other structures. It appears that of all titanates, thorates, zirconates, cerates, and stannates, $BaTiO_3$ and $PbTiO_3$ occupy a singular position, since the Ti-ion can move rather easily between its six nearest oxygen neighbors. This means that at the Ti-place a considerable ionic-displacement polarizability is localized, contributing to the term $\alpha^{(i)}$ in eq (2).

A third circumstance favoring a high value of the dielectric constant is the particular structure of the perovskites. It appears that the correction term that has to be added to the righthand side of eq (2) because of the insufficiently high symmetry of the perovskite lattice becomes considerable if at the place of the Ti-ion a polarizability is localized. Thus the "loosely bound" Ti-ion not only gives its "normal" contribution to $\alpha^{(i)}$ but also gives rise to a correction term, α_{cor}, which cannot be neglected.

If we accept the given interpretation of the high dielectric constant of $BaTiO_3$, we can easily show that a strong dependency on temperature is to be expected (*7*). In order to explain this dependency, the occurrence of permanent dipoles in the high temperature region has been assumed by some authors. We think, however, that such an assumption should not be made since the following simple argument can give a quantitative explanation.

Writing eq (2) with the correction term α_{cor} included as

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha, \tag{3}$$

where α stands for $\alpha^{(e)} + \alpha^{(i)} + \alpha_{\text{cor}}$, we find for the temperature coefficient

$$\frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial T} = \frac{(\varepsilon - 1)(\varepsilon + 2)}{3\varepsilon}\left\{\frac{1}{N}\frac{\partial N}{\partial T} + \frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right\}. \tag{4}$$

Putting $\frac{1}{N}\frac{\partial N}{\partial T} = -3\beta$ (β = coefficient of linear expansion) and approximating $\varepsilon - 1$ and $\varepsilon + 2$ by ε, we obtain from eq (4):

$$\frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial T} = \varepsilon\left\{-\beta + \frac{1}{3}\frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right\}, \tag{5}$$

$$\text{or } \varepsilon = \frac{1}{\left(\beta - \frac{1}{3}\frac{1}{\alpha}\frac{\partial \alpha}{\partial T}\right)(T - T_0)}, \tag{6}$$

where T_0 is an integration constant.

We have already seen that experiments above the transition temperature θ can be described by

$$\varepsilon = \frac{1}{\beta(T - \theta)} \tag{7}$$

From this it follows that

$$\frac{\partial \alpha}{\partial T} = 0, \tag{8}$$

and

$$T_0 = \theta. \tag{9}$$

The value of θ can be expressed in terms of the dielectric constant ε' measured at a temperature T' by

$$\theta = T' - \frac{1}{\beta(\varepsilon' + 2)} \tag{10}$$

It is to be noted that to eq (7) a factor must be added in order to correct for the porosity of the titanate samples. If we call ε_{exp} the measured value of the dielectric constant of a sample with a small amount p of spherical holes, eq (7) becomes

$$\varepsilon_{\text{exp}} = \frac{1 - \frac{3}{2}p}{\beta(T - \theta)}. \tag{7'}$$

As to eq (8), one might think that this equation is rather trivial. It is necessary, however, to discuss separately the temperature dependency of all three contributions to $\alpha = \alpha^{(e)} + \alpha^{(i)} + \alpha_{\text{cor}}$. It is well known that $\alpha^{(i)}$ increases with increasing temperature, since the restoring forces playing a part in the infrared vibrations of the lattice decrease owing to the thermal expansion of the crystal.

It can be expected that $\alpha^{(e)}$ also depends on temperature since we have found that for many simple ionic compounds like NaCl $\alpha^{(e)}$ shows a positive temperature coefficient (*8*).

It is difficult to predict the temperature dependency of α_{cor}. From eq (8) we can infer that $\frac{\partial \alpha_{\text{cor}}}{\partial T}$ cancels the effects of $\frac{\partial \alpha^{(e)}}{\partial T}$ and $\frac{\partial \alpha^{(i)}}{\partial T}$.

It is interesting to notice the analogy between

$$\chi_{\text{el}} = \frac{\varepsilon - 1}{4\pi} \approx \frac{\varepsilon}{4\pi} = \frac{1}{4\pi\beta(T - \theta)}, \tag{11}$$

where χ_{el} denotes the electric susceptibility, and Curie-Weiss's law for paramagnetics

$$\chi_{\text{magn}} = \frac{C}{T - \theta_m}. \tag{12}$$

(χ_{magn} = magnetic susceptibility, θ_m = Curie temperature).

It must be emphasized, however, that the similarity is only a formal one. In the electric case χ_{el} increases with decreasing T, since the number of polarizable particles per unit of volume increases (thermal contraction effect); in the magnetic case χ_{magn} increases with decreasing T, since the permanent magnetic moments can be more easily oriented (Boltzmann-factor effect).

All these considerations about polarizabilities and temperature-dependencies hold equally for mixed crystals of $BaTiO_3$ with other perovskites. Eq (10) enables us to explain the variation of the peak temperature θ with the composition of the mixed crystals. By substitution, by means of the corrected Clausius-Mosotti formula, we find

$$\theta = T' - \frac{1}{3\beta} + \frac{4\pi}{9\beta} N' \alpha', \tag{10'}$$

where N' and α' are the values of N and α at the temperature T'.

Since all the variables in this formula show only a small and (to a first approximation) linear dependency on the composition, we see at once that θ also varies linearly (Fig. 4). The variations of the product $N'\alpha'$ when replacing Ba by Sr are only small; because of the factor $\frac{1}{\beta}$, however, large effects on θ result.

The low temperature region. Let us consider a titanate dielectric below its transition point, and thus in the temperature region where spontaneous polarization occurs. In view of crystallographic considerations it is reasonable to ascribe this polarization mainly to a displacement of the Ti-ions from the centers of their octahedral interstices. Such an eccentric Ti-ion acts on its environment as if a Ti-ion were placed in the center, together with a dipole of moment equal to ionic charge × displacement. It is interesting to examine the interaction of such dipoles more closely. The Ti-ions are placed at the points of a simple cubic lattice; thus it is evident that the state of lowest energy should be a macroscopically unpolarized arrangement where alternating strings of dipoles occur, rather than a polarized arrangement where all dipoles are pointing in the same

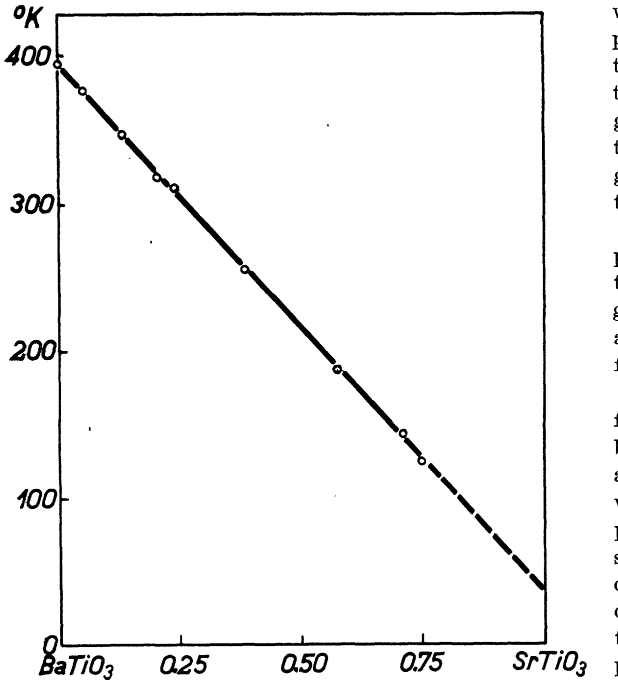

FIG. 4. Transition points of mixed crystals of barium and strontium titanate.

direction (*5*). It is possible, however, to understand why in the perovskite lattice the polarized state is favored. Let us consider a cross section through the lattice (Fig. 5). All Ti-ions are separated by easily polarizable O-ions, in which dipole moments can be induced by the Ti-dipoles. It is easily seen that a parallel orientation of a row of Ti-dipoles is favored by the oxygen ions *A*, which assume induced moments in the same direction. Such rows of parallel Ti-dipoles are coupled together by oxygen ions *B*, the moments in these oxygen ions pointing in the opposite direction. For other positions of the oxygen ions *B* such a coupling would not occur.[1] The particular properties of the perovskite structure making the spontaneous polarization possible also give rise to a favorable deviation from the formula of Clausius-Mosotti in the temperature region above θ. The infrared vibrations corresponding to tetragonal deformation have a small restoring force and give a large contribution to the ionic polarizability and thus to ε.

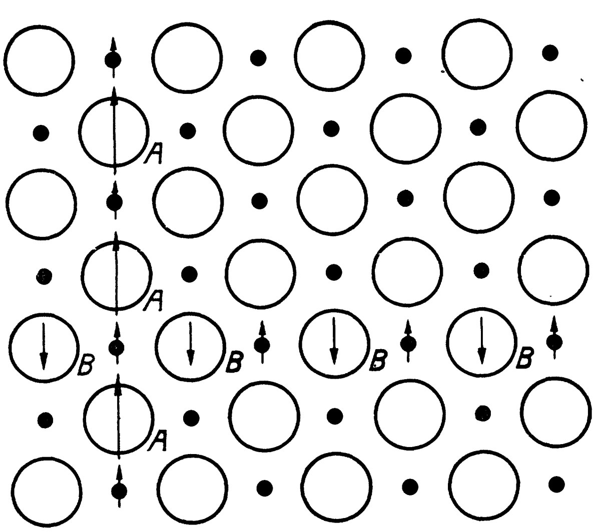

FIG. 5. Cross-section through the barium titanate lattice.

The transition temperature. Coming from high temperatures, the cubic form of $BaTiO_3$ becomes at a certain temperature unstable with respect to the polarized tetragonal form (*3*) (probably a first-order transition). There are two approaches to describing this transition, coming from the high and from the low temperature region.

In the first place it is to be noted that the restoring force just mentioned contains, besides positive contributions (e.g., the Born repulsion), negative contributions arising from the polarization of the lattice during the vibration. In view of the close relation between this polarization and ε, the negative contribution to the restoring force becomes increasingly important as ε increases by the contraction of the lattice, so that at a certain temperature the negative prevails over the positive contribution, and as the corresponding frequency approaches zero, a spontaneous deformation of the lattice occurs. At the same moment the dipoles, which play such an important role in the low temperature region, are formed by a shift of the titanium ions in the direction of the elongated *c*-axis.

On the other hand, we can start from the spontaneously polarized state. In ~~the section on the~~ low temperature region it was made plausible that the interaction between the Ti-dipoles takes place through the medium of the oxygen ions between them. Such an interaction must decrease as the lattice expands, so that at a certain temperature the energy of interaction becomes of the order of *kT* and the spontaneous polarization is destroyed.

It is difficult at the moment, however, to treat these problems quantitatively, since data concerning internal forces are rather scarce and particularly because the ionic picture used is only a zero-order approximation.

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[1] In the structure of the hexagonal form of $BaTiO_3$ proposed by Evans and Burbank (*1*), which shows a low dielectric constant, such an effect cannot occur, the rows of Ti-ions being interrupted.