SOVIET PHYSICS JETP VOLUME 6(33) NUMBER 2 FEBRUARY, 1958

RELAXATION POLARIZATION AND LOSSES IN NONFERROELECTRIC DIELECTRICS WITH HIGH DIELECTRICS CONSTANTS

G. I. SKANAVI, IA. M. KSENDZOV, V. A. TRIGUBENKO, and V. G. PROKHVATILOV

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor November 22, 1956

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 320-334 (August, 1957)

It is shown that in polycrystalline dielectrics of the $SrTiO_3 - Bi_2O_3 \cdot nTiO_2$ systems, over a wide range of concentration of the components, there occurs a relaxation polarization that leads to a very high dielectric constant without ferroelectric properties. The nature of the relaxation polarization changes upon change of the relative amounts of the components. Three classes of strontium-bismuth titanates have been established, which differ in composition, crystal structure, and properties. Dielectrics of the first class have the perovskite structure; they may be divided into two groups that have different types of relaxation polarization. For the first group, as was shown earlier,[1] the dielectric constant is close to 1000; for the second group ϵ reaches 6000 over a quite broad frequency range. The frequency and temperature dependence of ϵ and of $\tan \delta$ are studied in relation to the composition and structure of the new dielectrics. The experimental results are interpreted on the basis of ideas about ionic relaxation polarization.

1. STATEMENT OF THE PROBLEM

IT was shown by Skanavi and Matveeva[1] that the conjunction of two factors — an internal field favoring polarization, which results from the perovskite structure, and a large ionic relaxational polarizability, which occurs in the presence of vacant sites in the lattice — leads to a very high dielectric constant without ferroelectric properties.

The object of the present research was a more detailed experimental study of the laws of relaxational polarization, not only for the strontium-bismuth titanate (SBT-1) studied in Ref. 1, but also — as far as possible — for all dielectrics of the $SrTiO_3 - Bi_2O_3 \cdot nTiO_2$ systems, with variation of the relative amounts of the components. Our intention was to trace the influence of changes of crystal structure in general, and of the number of vacant sites in particular, on the nature of the relaxational polarization and on the magnitude of the fundamental characteristics (dielectric constant, loss angle, etc.). Such an experimental study was of interest both for confirmation of some of the ideas of Ref. 1, and for elucidation of methods of obtaining new dielectrics with specified properties.

2. SAMPLES AND METHODS OF INVESTIGATION

The samples studied for this purpose were polycrystalline dielectrics of the systems $SrTiO_3 - Bi_2O_3 \cdot 2TiO_2$, $SrTiO_3 - Bi_2O_3 \cdot 3TiO_2$, and $SrTiO_3 - Bi_2O_3 \cdot 4TiO_2$, with wide variation of the relative amounts of the components. They were progressively synthesized at temperatures 1000, 1100, 1200, and 1300°C and were finally fired until there were no exposed pores. The structure of these dielectrics was studied with x-rays, their densities and the numbers of atoms in the unit cell were determined, and the dielectric constants ϵ and loss tangents $\tan \delta$ were measured as functions of temperature and frequency. For the density measurement, the samples were pulverized in an agate mortar until the particle dimensions were 2 to 7 μ; this was known to be less than the mean dimensions of the air spaces in the samples. The density was determined by means of a pycnometer 5 cm^3 in volume; toluene was used, after preliminary evacuation. The crystal lattice parameters were determined from a Debye pattern taken with a camera 114.6 mm in diameter. An asymmetric method was used, with copper radiation and a nickel filter. This was done by one of the authors and also, at our request, by N. A. Porai-Koshits; the results of the two determinations agreed. The relative intensities were measured with roentgenograms automatically traced on a URS-50I ionization assembly.

The values of ϵ and $\tan \delta$ were measured over a wide range of temperatures and frequencies by means of standard bridge and resonance apparatus. The measurements in the frequency interval 40 to 180 Mc were of preliminary nature, being subject to comparatively large errors.

3. EXPERIMENTAL RESULTS

A. Structural Properties of Strontium-Bismuth Titanates

The results of the x-ray analysis show that all the strontium-bismuth titanate systems studied may be divided into at least three basic classes. In the first class, with high concentrations of strontium titanate, solid solutions form, with a cubic lattice of perovskite type. In the system $SrTiO_3 - BiTiO_{7/2}$, or $SrTiO_3 - 1/2\ (Bi_2O_3 \cdot 2TiO_2)$, the solid-solution range is bounded by a concentration of 25 to 28 mol percent, in the system $SrTiO_3 - Bi_{2/3}TiO_3$ by 35 mol percent, and in the system $SrTiO_3 - Bi_{1/2}TiO_{11/4}$, by 30 mol percent, of the respective bismuth titanates. In the second class (with high concentrations of bismuth titanate) there is a broad range of mixtures of a solid solution of perovskite type with a new crystalline phase of complex structure, corresponding to chemical compounds of strontium titanate with bismuth titanate (for example, $SrBi_2Ti_4O_{12}$). For the third class, with small concentrations of $SrTiO_3$ (less than about 30 mol percent), the Debye patterns are very complicated; they contain, together with other lines, the lines of bismuth titanate.

In the solid-solution range (class 1), for all three systems, the lattice has a cubic structure with the parameter $a = 3.898 \pm 0.002$ A. In these systems there is a possibility of formation of two types of solid solution: a substitutional solid solution, and a solid solution with a structural defect of subtractive type. The radii of the bismuth and strontium ions are very nearly equal (~ 1.2 A); it is therefore to be expected that a bismuth ion in a solid solution will be able to occupy sites only in the strontium portion of the lattice, in which case the lattice constant need not change. For formation of a substitutional solid solution, a reaction must proceed, in which oxides dissociate with liberation of gaseous oxygen and lowering of the valence of the Bi or Ti; for instance, when n = 2 the scheme is the following:

$$x\,SrTiO_3 + (1-x)\,BiTiO_{7/2} \rightleftarrows (Sr_xBi_{1-x})TiO_3 + {}^{1}/_{4}\,(1-x)\,O_2\uparrow + (1-x)\,(e), \tag{1}$$

where x is the molecular concentration of $SrTiO_3$, and where (e) is a quasi-free electron that results from liberation of oxygen. It is clear that such a reaction is promoted by the high firing temperature (above 1450°C) that is necessary for complete sintering of materials containing less than 10 molar percent of bismuth titanate. At lower sintering temperatures (≤ 1450°C, materials with high concentration of bismuth titanate), dissociation of oxides is less probable, and subtraction solid solutions may form.

Depending on the number n in the formula $Bi_2O_3 \cdot nTiO_2$, vacant sites may form in the strontium part of the crystal lattice, in the strontium and titanium parts, or in the strontium and oxygen parts, in accordance with the following schemes: for n = 2, for example,

$$x\,SrTiO_3 + (1-x)\,BiTiO_{7/2} \rightarrow (Sr_xBi_{1-x})\,TiO_3 \cdot {}^{1}/_{6}\,(1-x)\,Sr^*Ti^*O_3, \tag{2}$$

where the asterisk after the symbol for the element represents a corresponding vacant site; for n = 3,

$$x\,SrTiO_3 + (1-x)\,Bi_{2/3}TiO_3 \rightarrow (Sr_xSr^*_{1/3\,(1-x)}\,Bi_{2/3\,(1-x)})\,TiO_3; \tag{3}$$

and for n = 4,

$$x\,SrTiO_3 + (1-x)\,Bi_{1/2}TiO_{11/4} \rightarrow (Sr_xSr^*_{1/2\,(1-x)}\,Bi_{1/2\,(1-x)})\,Ti\,(O_{1/4\,(11+x)}O^*_{1/4\,(1-x)}). \tag{4}$$

To test whether vacant sites are actually formed in the crystal lattice when the sintering temperature is not very high, the number of atoms in the unit cell was determined from the experimental data on density and lattice parameter, by the known formula

$$N = Vd/A \cdot 1.65 \cdot 10^{-24}, \tag{5}$$

where d is density, V is the volume of the unit cell, and A is the mean atomic weight, calculated from the proportions of the materials [left sides of formulas (2) to (4)]. In Table I the number of atoms in the unit cell, obtained in this way, is compared with the number of atoms in the unit cell, directly calculated from the right sides of formulas (2) to (4).

The data of Table I show that the number of atoms in the unit cell of the solid solutions decreases with increase of the concentration of bismuth titanate. This indicates the formation of a solid solution of the second kind, of subtractive type; however, the decrease proceeds more rapidly than it should according to the right side of formulas (2) to (4). This makes it impossible to determine the type of vacant sites.

Therefore for determination of the most probable type of vacant sites, a roentgenographic method was used. Because of the large difference between the atomic scattering factors of Sr^{2+} and Bi^{3+}, one can infer the type of solid solution from the change in the intensity of the reflections. Calculations of the relative intensities were carried out for the space group $O'_h - P_m3m$ for all three systems, under the condition that the Bi ions occupy sites in the strontium part of the lattice and that the number of vacant sites for each system is determined by the right side of formulas (2) to (4). Table II gives a comparison of the relative intensities of various reflections, as obtained experimentally, with the calculated values, for the compositions with the largest concentrations of bismuth titanate among those listed in Table I.

TABLE I

System	Composition	Density g/cm³	Number of atoms in unit cell	
			From (5)	Calc. by (2)-(4)
	$SrTiO_3$	5.04	4,97	5.0
$SrTiO_3-Bi_2O_3\cdot 2TiO_2$	0,9 $SrTiO_3$+0.1 $BiTiO_{7/2}$ 0,8 $SrTiO_3$+0.2 $BiTiO_{7/2}$ 0,7 $SrTiO_3$+0.3 $BiTiO_{7/2}$	5.31 5.46 5.54	4,90 4,80 4.67	4,975 4,943 4,920
$SrTiO_3$— $Bi_2O_3\cdot 3TiO_2$	0,9 $SrTiO_3$+0.1 $Bi_{2/3}TiO_3$ 0,8 $SrTiO_3$+0.2 $Bi_{2/3}TiO_3$ 0,7 $SrTiO_3$+0.3 $Bi_{1/3}TiO_3$	5,19 5.32 5.36	4,90 4,83 4,73	4,966 4,933 4,900
$SrTiO_3$— $Bi_2O_3\cdot 4TiO_2$	0.7 $SrTiO_3$+0.3 $Bi_{1/3}TiO_{11/4}$	5.25	4.79	4.775

TABLE II

hkl	$J_{hkl} : J_{200}$					
	0.7 $SrTiO_3$+0,3 $BiTiO_{7/2}$		0.7$SrTiO_3$+0.3$Bi_{2/3}TiO_3$		0.7$SrTiO_3$+0,3$Bi_{1/2}TiO_{11/4}$	
	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.
100	31	17	19	17	9	19
110	227	236	205	196	191	228
111	78	72	70	61	64	68
200	100	100	100	100	100	100
210	17	13	9,7	7,7	5,6	8,1
211	68	82	77	76	71	92
220	59	40	59	46	59	58
300,221	8,5	4.0	5.0	5,6	2,5	6,5
310	36	32	32	27	30	34
311	24	8.5	19	9.0	19	8.6
222	19	16	19	22	18	16
321	48	37	43	42	40	39
400	11	6.3	11	9	11	11
300,411	34	22	30	22	29	30

The intensity of the (200) reflection was taken as 100% intensity; it had the largest structure factor. Among the various reflections, the ones that are most sensitive to changes of intensity, upon replacement of strontium by bismuth and formation of vacant sites, are those for which the structure amplitudes of the titanium and oxygen have a sign opposite to that of the structure amplitudes of the strontium and bismuth. In Table II, such reflections are (100), (210), and (300, 221). Comparison of the calculated and experimental intensities of these three most "sensitive" reflections shows that the best agreement occurs for the solid solution of composition $0.7SrTiO_3 + 0.3Bi_{2/3}TiO_3$, corresponding to the $SrTiO_3 - Bi_2O_3{\cdot}nTiO_2$ system in which vacant sites should form only in the strontium part of the lattice.

However, as Table II shows, we may infer that a similar situation occurs also in the other systems at concentrations that correspond to the range of solid solutions of subtractive type (group a of structural class 1). In fact, the experimentally determined intensities of the "sensitive" reflections for the systems $SrTiO_3 - Bi_2O_3{\cdot}2TiO_2$ and $SrTiO_3 - Bi_2O_3{\cdot}4TiO_2$ differ little (30% or less) from the calculated intensities of the same reflections for the system $SrTiO_3 - Bi_2O_3{\cdot}3TiO_2$. Therefore, for example, upon sintering of samples of the system $SrTiO_3 - Bi_2O_3{\cdot}2TiO_2$ there must occur a liberation (and escape) of surplus Bi_2O_3. Just this phenomenon is observed experimentally and is confirmed by the results of a chemical analysis, made at our request by E. D. Borneman and O. A. Alekseeva.*

Thus we may expect the nature of the polarization of dielectrics of all three systems, within the bounds of group a of structural class 1, to be similar; for we may suppose with a high degree of probability that in these systems solid solutions of subtractive types form, with vacant sites in the strontium part of the lattice.

---

*The authors express their gratitude to E. D. Borneman and O. A. Alekseeva for this work.

B. Dielectric Properties of Dielectrics of the Systems $SrTiO_3 - Bi_2O_3{\cdot}nTiO_2$

Some of the results of numerous measurements are given in Figs. 1 to 5.

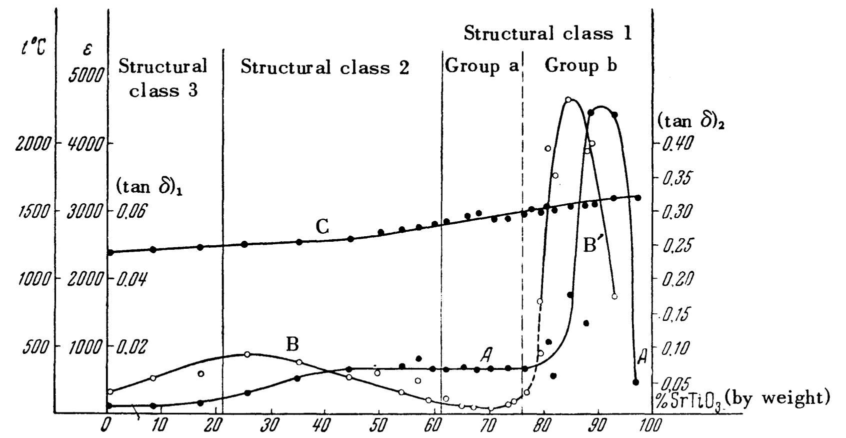

FIG. 1. Dependence of ϵ (curve A) and tan δ (curve B, scale 1; curve B', scale 2), at room temperature and at frequency 1.5 megacycles/sec, and also of sintering temperature (curve C), on $SrTiO_3$ content, in a batch of dielectrics of the system $SrTiO_3 - Bi_2O_3{\cdot}2TiO_2$.

From Fig. 1 it is evident that for n = 2, the dielectric constant and loss angle at frequency 1.5 megacycles and room temperature attain widely different values, according to the structure of the materials obtained. For the first structural class, the dielectric constant is about 1000 at concentrations of $Bi_2O_3{\cdot}2TiO_3$ greater than 15% by weight (group a); it reaches 5000 to 6000 at smaller concentrations of $Bi_2O_3{\cdot}2TiO_2$ (group b).

The loss angle is inconsequential for materials of group a and increases abruptly for materials of group b. The increase of ϵ and tan δ in materials of group b is accompanied by a change of color from light cream (group a) to dark gray (group b). For structural classes 2 and 3, the the dielectric constant decreases markedly with decrease of $SrTiO_3$ content, and tan δ undergoes an increase. Similar dependence of ϵ and tan δ on concentration is observed in the other systems (n = 3, n = 4). From Fig. 2 it is evident that the polarization of the solid solutions of the system $SrTiO_3 - Bi_2O_3{\cdot}3TiO_2$ (as is also true of the other systems) is of relaxational type. With increase of the concentration of bismuth titanate, the temperatures at the maxima of ϵ and of tan δ increase (curves 1, 2, and 3 of Fig. 2). For the first structural class (large concentrations of bismuth titanate, curves 4 and 5 of Fig. 2), ϵ decreases with increase of the bismuth titanate content, but the temperature of maximum ϵ remains practically unchanged. Fig. 3 illustrates the clearly expressed relaxational nature of the polarization of these solid solutions. It is clear that with increase of frequency, the temperatures of maximum ϵ and tan δ for a given material increase systematically. At sufficiently high temperatures, the values of ϵ for different frequencies agree.

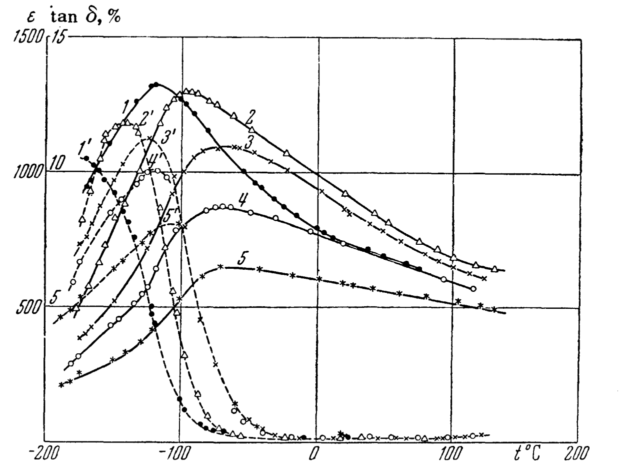

FIG. 2. Dependence of ϵ (curves 1—5) and tan δ (curves 1' — 5') on temperature for dielectrics of the system $SrTiO_3 - Bi_2O_3{\cdot}3TiO_2$, at frequency 1000 cps. 1 and 1', dielectric of composition 0.9 $SrTiO_3$ + 0.1 $Bi_{2/3}TiO_3$; 2 and 2', dielectric of composition 0.8 $SrTiO_3$ + 0.2 $Bi_{2/3}TiO_3$; 3 and 3', dielectric of composition 0.7 $SrTiO_3$ + 0.3 $Bi_{2/3}TiO_3$; 4 and 4', dielectric of composition 0.6 $SrTiO_3$ + 0.4 $Bi_{2/3}TiO_3$; 5 and 5', dielectric of composition 0.5 $SrTiO_3$ + 0.5 $Bi_{2/3}TiO_3$.

The polarization retains its relaxational character also for solid solutions with small bismuth titanate content (for example, group b for n = 2, Fig. 4). However, the temperatures of maximum ϵ and tan δ change faster with increase of frequency than is the case at larger concentrations of bismuth titanate.

The value of ϵ for solid solutions of group a, at room temperature, remains practically unchanged up to frequency 5×10^7 cps; it decreases at higher frequencies. The loss angle of dielectrics of this group rises sharply in the frequency range 10^6 to 10^8 cps. Upon increase of the concentration of bismuth titanate in the solid solutions, the frequency corresponding to the sharp rise of tan δ decreases. At bismuth titanate concentrations below 10 mol percent (group b), the dispersion of ϵ and the maximum of tan δ are located in a lower frequency range (Fig. 5).

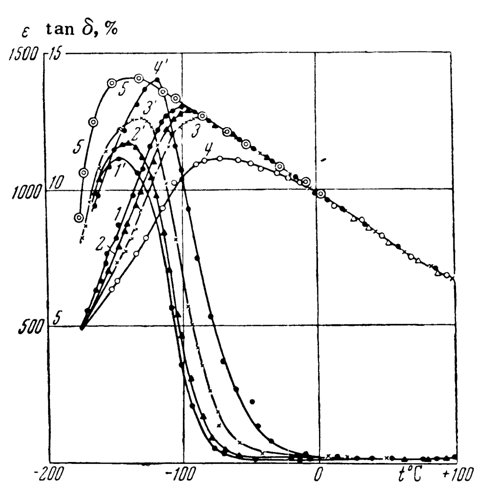

FIG. 3. Dependence of ϵ (curves 1 — 5) and tan δ (curves 1' — 4') of solid solution of composition 0.7 $SrTiO_3$ + 0.3 $Bi_{2/3}TiO_3$ on temperature for various frequencies. 1 and 1', frequency 4×10^2 cps; 2 and 2', frequency 10^3 cps; 3 and 3', frequency 5×10^3 cps; 4 and 4', frequency 2.5×10^5 cps; 5, frequency ~ 0.2 cps. At frequency ~ 0.2 cps and for temperatures above 0°C, there begins an increase of ϵ with temperature, not shown in the figure, due apparently to high-voltage polarization.

The experiments showed, as was expected, that the polarization of dielectrics of group a of structural class 1 for all three systems (n = 2, 3, 4) has a clearly expressed relaxational character. A slight diversity is manifest only in the absolute values of ϵ and tan δ in relation to the excess of Bi_2O_3 or TiO_2 in the systems n = 2 and n = 4. An important point is that the solid solutions of structural group a have a low conductivity, independent of field strength, whereas solid solutions of group b (samples of dark color) have a high conductivity that increases rapidly with increase of the field intensity (Fig. 6).

For materials of structural class 2 (the region of mechanical mixtures), an increase of bismuth titanate concentration produces not only a decrease of the magnitude of ϵ, but also a decrease of the frequency at which a decrease of ϵ is observed (Fig. 7); this suggests the possibility that a relaxational process is present in this concentration range as well. Further evidence of this is the temperature dependence of ϵ and tan δ at various frequencies.

For all the materials studied, no dielectric hysteresis loops were detected at temperatures above or below the maximum of ϵ.

The experimental results presented show that a high dielectric constant can be obtained in solid solutions by combining a favorable crystal structure with a relaxational polarization resulting from vacant sites in the lattice. These vacant sites can be obtained by formation of a solid solution of the second kind, of subtractive type, which is produced by replacement of some of the cations of the lattice with cations of higher valence. It should be mentioned that relaxational polarization can occur also in lattices of fluorite type, through formation of subtraction solid solutions ($ZrO_2 \cdot MgO$, $ZrO_2 \cdot CaO$); in this case, however, it does not, of course, lead to a high value of the dielectric constant, since the fluorite structure does not favor this.

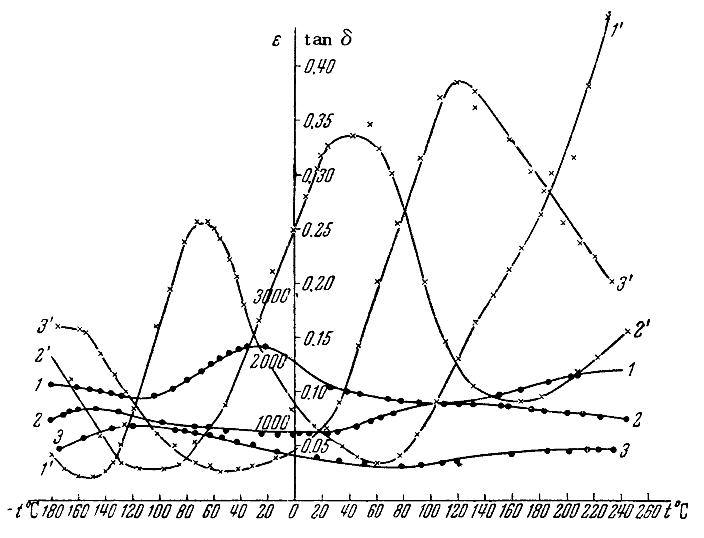

FIG. 4. Dependence of ϵ and tan δ on temperature for a dielectric of batch composition $SrTiO_3$ 77% and $Bi_2O_3 \cdot 2TiO_2$ 23% by weight, at various frequencies. 1 and 1', ϵ and tan δ at frequency 10^3 cps; 2 and 2', ϵ and tan δ at frequency 90 kcs; 3 and 3', ϵ and tan δ at frequency 1.5 Mcs.

Our work has shown that the general method of obtaining dielectrics with a high dielectric constant, without ferroelectric properties, is applicable also to other compounds with the perovskite structure. Introduction of bismuth titanate into $BaTiO_3$ [$BaTiO_3 — Bi_2O_3 \cdot nTiO_2$] leads to a change in the nature of the polarization. With increase of the bismuth titanate concentration in this system to 15 mol percent, the spontaneous polarization gives way to a relaxational. At concentrations of less than 15 mol percent of 1/2 ($Bi_2O_3 \cdot 2TiO_2$), spontaneous polarization still occurs, but the Curie point moves to lower temperatures (curves 1 and 2 of Fig. 8). After the transition to relaxational polarization (bismuth titanate concentration greater than 15 mol percent), the peak in ϵ is washed out, and the temperature corresponding to this peak increases with increasing concentration (curves 4 and 5 of Fig. 8), just as in the system $SrTiO_3 — BiO_3 \cdot nTiO_2$. The presence of relaxational polarization is confirmed by the shift of the temperatures of maximum ε and tan δ with change of frequency (Fig. 9), which is not observed in ferroelectrics; also by the absence of dielectric hysteresis at all temperatures, and by the fact that ε is independent of the field intensity.

4. DISCUSSION OF EXPERIMENTAL RESULTS

It has been established experimentally that in the solid solutions $SrTiO_3 - Bi_2O_3 \cdot nTiO_2$ and $BaTiO_3 - Bi_2O_3 \cdot 2TiO_2$, at sufficient concentrations of bismuth titanate, a high dielectric constant is produced by a combination of favorable structure and of relaxational polarization, which occurs when vacant sites are present. We may suppose that the relaxational polarization originates from relatively large displacements of weakly bound ions, which by thermal motion surmount local potential barriers; for the bonds in the crystal lattices are predominantly of ionic nature. It is difficult to suppose that the large ions Ba^{2+}, Sr^{2+}, Bi^{3+}, or O^{2-} are capable of displacements through such a large distance, since they are densely packed in the lattices. The possibility that appears most plausible is that the large displacements are those of Ti^{4+} ions, whose dimensions are small. Formation of vacant sites in the strontium or barium parts of the lattice will lead to a shift of the equilibrium positions of the oxygen ions, i.e., to distortion of the oxygen octahedra that surround the titanium ions, and consequently to the appearance of several local minima of the potential energy of a titanium ion.

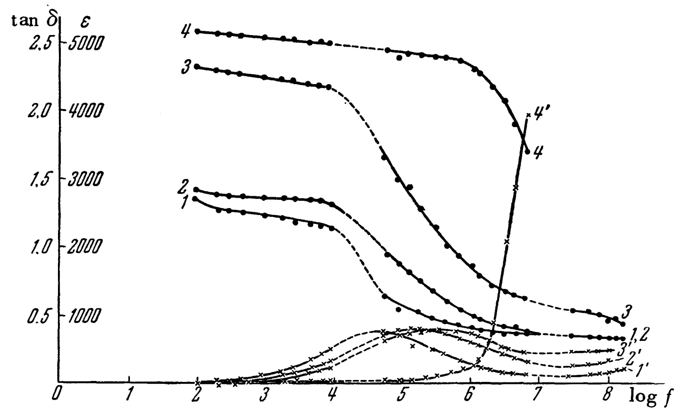

FIG. 5. Dependence of ε (curves 1 — 4) and tan δ (curves 1′ — 4′) on frequency (in cps) at room temperature, for dielectrics of the system $SrTiO_3 - Bi_2O_3 \cdot 2TiO_2$ with small bismuth titanate content. $SrTiO_3$ content (by weight): 1 and 1′, 77%; 2 and 2′, 79%; 3 and 3′, 85%; 4 and 4′, 93%.

At small concentrations of bismuth titanate (less than 15 mol percent) and at high sintering temperatures, solid solutions of substitutional type are formed, with liberation of oxygen and formation of quasi-free electrons (formula 1). With this, clearly, there also occur the experimentally observed change of color (darkening) of the specimens, which is linked with absorption in the visible part of the spectrum, and an increase of the electronic electrical conductivity. At the same time the dielectric constant and tan δ increase sharply, and the polarization, in the frequency and temperature range investigated, is of relaxational nature. This may be connected either with a heterogeneous microstructure of the polycrystalline dielectrics (the presence of phases of different conductivities must lead to relaxation of Maxwellian type) or with formation of F-centers with large orbital radii (a quasi-free electron bound by electrostatic forces, for example to a bismuth ion, will also be at a comparatively large distance from it). A unique answer to this question requires further investigations. In the case of solid solutions with vacant sites (SBT-1), it is very probable — as has been shown — that the relaxational polarization is ionic in nature; and analysis of the data by means of a simple model makes it possible to estimate a number of quantities characteristic of the ionic relaxation.

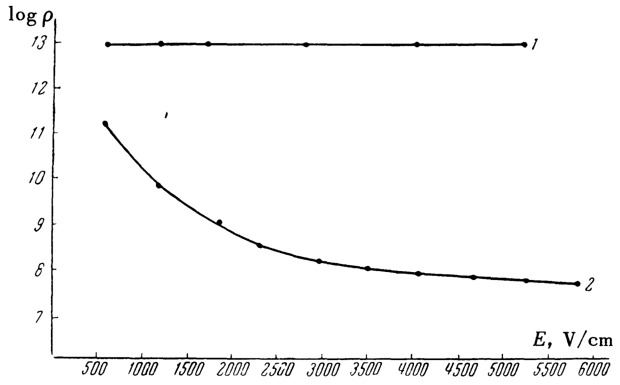

FIG. 6. Dependence of the logarithm of the specific resistance (in ohm cm) on the field intensity at room temperature, for strontium-bismuth titanates of batch composition (by weight): 1, $SrTiO_3$ 55%, $Bi_2O_3 \cdot 2TiO_2$ 45%; 2, $SrTiO_3$ 93%, $Bi_2O_3 \cdot 2TiO_2$ 7%.

As Landau remarked, it follows from simple phenomenological considerations that the relaxation time of the polarization is larger, the higher the static dielectric constant ϵ_0.* In fact, if we expand the mean

---

*We shall show shortly that any molecular theory of relaxational polarization also gives, in general, this same result.

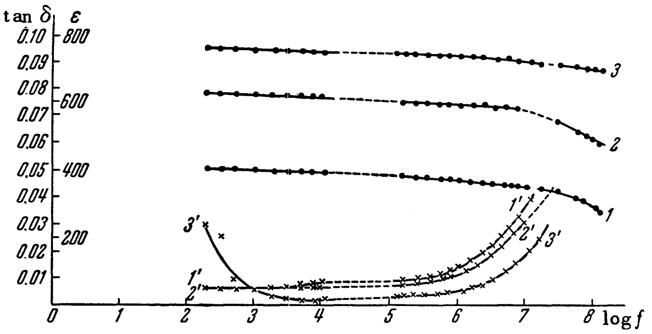

FIG. 7. Dependence of ϵ (curves 1 — 3) and tan δ (curves 1′ — 3′) of frequency (in cps) at room temperature, for strontium-bismuth titanates. 1 and 1′, batch composition (by weight) $SrTiO_3$ 26%, $Bi_2O_3 \cdot 2TiO_2$ 74%;) 2 and 2′, $SrTiO_3$ 35%, $Bi_2O_3 \cdot 2TiO_2$ 65%; 3 and 3′, $SrTiO_3$ 55%, $Bi_2O_3 \cdot 2TiO_2$ 45%.

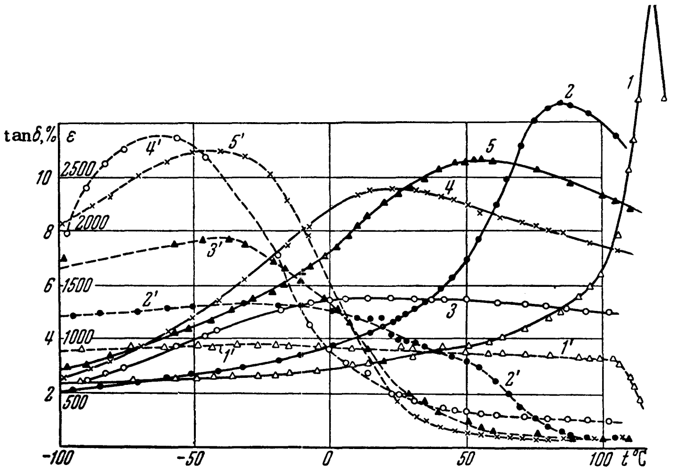

FIG. 8. Dependence of ϵ and tan δ on temperature at frequency 1000 cps, for dielectrics of the system $BaTiO_3 - BiTiO_{7/2}$: 1, 0.95 $BaTiO_3$ + 0.05 $BiTiO_{7/2}$; 2, 0.9 $BaTiO_3$ + 0.1 $BiTiO_{7/2}$; 3, 0.85 $BaTiO_3$ + 0.15 $BiTiO_{7/2}$; 4, 0.7 $BaTiO_3$ + 0.3 $BiTiO_{7/2}$.

field intensity as a series in the frequency,

$$E_{\text{av}} = \frac{4\pi I}{\varepsilon_0 - 1} + 4\pi\alpha' \dot{I} + 4\pi\beta' \ddot{I} + \ldots \qquad (5')$$

(I is the polarization, or electric moment of unit volume), and retain only three terms of this series, we get

$$\begin{aligned} \varepsilon^* &= 1 + (\varepsilon_0 - 1)[1 + i\omega(\varepsilon_0 - 1)\alpha' - \beta'(\varepsilon_0 - 1)\omega^2]^{-1}, \\ \varepsilon' &= 1 + (\varepsilon_0 - 1)\,[1 - \beta'(\varepsilon_0 - 1)\,\omega^2]\,\{[1 - \beta'(\varepsilon_0 - 1)\,\omega^2]^2 \\ &\quad + \omega^2(\varepsilon_0 - 1)^2\,\alpha'^2\}^{-1}, \end{aligned} \qquad (6)$$

where $(\epsilon_0 - 1)\,\alpha' = \theta$ is the relaxation time of the polarization.

In this case, $\epsilon' \rightarrow 1$ at high frequencies. However, a great quantity of experimental data for polar liquids and for crystals that contain dipolar groups[3] shows that the dielectric constant diminishes sharply as the frequency increases over a very limited interval, and remains practically independent of frequency outside that interval. At sufficiently low frequencies ϵ' is close to ϵ_0; at sufficiently high frequencies, $\epsilon' \rightarrow \epsilon_\infty > 1$.

As has been shown, in the solid solutions SBT-1 a partial replacement of strontium ions by bismuth ions not only increases the dielectric constant, but sharply changes the nature of its dependence on temperature and frequency. For sufficiently high frequencies, $\epsilon_\infty \sim 250$; but $\epsilon_0 > 1000$. It is clear that simple phenomenological considerations [formula (6)] are not sufficient for the interpretation of the relations that have been established.

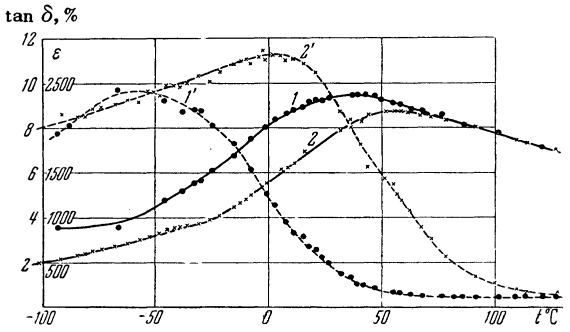

FIG. 9. Dependence of ϵ and tan δ on temperature for a dielectric of batch composition 0.8 $BaTiO_3$ + 0.2 $BiTiO_{7/2}$; 1, f = 10^3 cps; 2, f = 5×10^5 cps.

In this connection, "model" interpretations of the nature of the relaxational polarization in SBT-1 acquire some additional basis; the more so, because it was considerations of precisely this type that led to the creation of these new dielectrics. The starting point here is the separation of the polarization into two parts: (a) a polarization (ionic, electronic) that becomes established rapidly, and (b) a polarization that becomes established comparatively slowly and that depends comparatively strongly on temperature — the so-called relaxational polarization, which (like the first part) is proportional to the field; for the ϵ' of the dielectrics SBT-1 is independent of the field intensity even at strong fields. In contrast to the polarization of polar liquids and of crystals containing dipolar groups, the first part of the polarization is due not only to electronic displacements but also to ordinary elastic displacements of ions; and the relaxational polarization is due not to orientation of dipolar groups, but to passage of some of the ions across local potential barriers.

It must be stressed that such a separation of the complete polarization into a part that is established in a short time and a part that is established slowly, regardless of the mechanism of polarization, always leads to a formula of Debye type for the dependence ϵ' and ϵ'' (and consequently also of tan δ) on frequency and temperature. Since the effective field for dense phases is not equal to the macroscopic mean field, the relaxation time of the slowly established polarization is always approximately proportional to the static dielectric constant; this is in agreement with the simple phenomenological considerations presented above. Such an approach to the treatment of experimental data, in contrast to the phenomenological, provides a possibility of giving the coefficients in the series (5′) a descriptive interpretation and of determining to what degree one or another mechanism of relaxational polarization agrees with experimental data. The "model" method of treating experimental data usually encounters difficulty with regard to the calculation of the deviation of the effective (local) field from the mean field. However, when the experimental data are well described by a formula of Debye type, as is true in the case under consideration, it is possible to circumvent this difficulty by introducing the so-called mean or generalized internal-field coefficients β_1 and β_2.[1,3]

It should be mentioned that formulas of Debye type coincide with formulas (6), obtained from the series (5′), if in the latter we keep only the first two terms instead of three, and if we set ϵ_∞ equal to unity. Then the polarization relaxation time is $\theta = (\epsilon_0 - 1)\,\alpha'$. As is well known, formulas of Debye type always give temperature-frquency maxima of tan δ, and also a temperature maximum of ϵ' at given frequency; as was pointed out above, these are observed in all the new dielectrics obtained and investigated in this research. It is noteworthy that the frequency shifts of the curves of temperature variation of ϵ' and tan δ of the solid solutions SBT-1, as observed experimentally, correspond to a large diminution of polarization relaxation time θ with increase of temperature, since the curves move toward higher temperatures upon increase of frequency. However, this diminution of θ can not be attributed solely to decrease of ϵ_0. For example, upon increase of the temperature by 100°, the frequency corresponding to the temperature maxima and tan δ and ϵ' increases by four orders of magnitude. Thus it follows from the experimental data that the coefficient α' in the series (5′) decreases rapidly (almost exponentially) with temperature. In a model theory this corresponds to an exponential decrease with temperature of the relaxation time τ of weakly bound ions, which is proportional to θ; the coefficient of proportionality depends on ϵ_0 and ϵ_∞. If we use the generalized internal field coefficients,

$$\theta = \frac{\varepsilon_0 - 1 + 4\pi / \beta_1}{\varepsilon_\infty - 1 + 4\pi / \beta_1}\tau; \quad \tau = Ce^{U/kT}, \tag{7}$$

Here U is the activation energy; β_1 is the coefficient of proportionality between the electric moment of unit volume produced by relaxation polarization alone and its contribution to the mean local (internal) field; C is a quantity of the order of the reciprocal of the frequency of oscillation of the weakly bound ions about an equilibrium position and is only slightly dependent on temperature. By comparing the conditions for a temperature maximum of tan δ and of ϵ' at frequency ω, or by considering the shift of the temperature maximum of tan δ with change of frequency, it is possible to calculate the value of the activation energy of the weakly bound ions responsible for the relaxational polarization, by the following formulas.

In the first case

$$U \approx \frac{kT_1 T_2}{T_1 - T_2} \ln\left[\frac{\varepsilon'_{\max} - \varepsilon_\infty}{\varepsilon''_1} \frac{T_1}{T_2} \sqrt{\frac{\varepsilon_{02}}{\varepsilon_\infty}}\right], \tag{8}$$

under the condition that $(T_1/T_2) - 1 \ll (\epsilon'_{\max} - \epsilon_\infty)^2 kT_1^2/2\epsilon_1''^2\, UT_2$, where T_1 and T_2 are the temperatures of maximum ϵ' and of maximum tan δ; $\epsilon''_1 = \epsilon'_{\max} \tan\delta_1$ at temperature T_1; and ϵ_{02} is the static dielectric constant at temperature T_2.

In the second case

$$U = \frac{kT_2^* T_2^{**}}{T_2^{**} - T_2^*} \ln\left[\frac{\omega^{**} T_2^* D^{*2}}{\omega^* T_2^{**} D^{**2}} \sqrt{\frac{\varepsilon_{0T_2^*}}{\varepsilon_{0T_2^{**}}}}\right], \tag{9}$$

where $D = (\epsilon'_{\max} - \epsilon_\infty)/\epsilon''_1$; the symbols * and ** refer to frequencies ω* and ω**.

Table III gives the original experimental data for one of the solid solutions of group a (SBT-1, Fig. 3) and the values of the activation energy of the weakly bound ions, as obtained from (8) with $\epsilon_\infty = 250$.

TABLE III

f, cps	T_1 °K	T_2 °K	ε'max	ε_{01}	ε_{02}	tan δ_1	ε''_1	U, ev
400	173	128	1310	1330	1450	0.033	43.2	0.19
1000	178	133	1290	1310	1420	0.030	38.7	0.20
5000	183	143	1260	1300	1400	0.038	47.8	0.23
$2.5\cdot10^5$	200	156	1110	1220	1380	0.037	41.1	0.26

The values of ϵ_{01} and ϵ_{02} given in Table III were obtained by extrapolation to temperatures T_1 and T_2 of the straight line that describes the dependence of ϵ' on temperature for $T > 273$°K. The values of activation energy calculated from (8) for different frequencies are close, but they increase slightly with increase of frequency. The values of U found with formula (9) from the experimental data of Table III, for various pairs of frequencies, lie within the limits 0.34 to 0.55 ev and likewise increase of frequency. The appreciable scattering of the calculated values of U, their increase with frequency, and also the increase of tan $\delta_{\max}$ with increase of frequency (Fig. 3), may be attributed to the presence of two or more sets of potential barriers and relaxation times; these were not taken into account in the calculations. The mean value of U depends comparatively slightly on the composition of the solid solutions SBT-1. However, upon increase of the bismuth titanate concentration the relaxation time at given temperature and consequently the activation energy increase slightly (Fig. 2). From knowledge of U it is possible to estimate the internal-field coefficient β_1 from the approximate relation

$$\left(\frac{\varepsilon'_{\max}-\varepsilon_\infty}{\varepsilon''_1}\right)^2 \approx \frac{2U}{kT_1}\cdot\frac{\beta_1(\varepsilon_\infty-1)+4\pi}{\beta_1(\varepsilon_{01}-1)+4\pi}. \tag{10}$$

It is found that for the solid solutions SBT-1, β_1 has a very small value ($\beta_1 \to 0$ or $\beta_1 = -10^{-2}$). The relaxation time of the weakly bound ions at temperature T_1 can be estimated, for example, by means of the following approximate formula (for $U \gg kT_1$):

$$\omega\tau_1 \approx kT_1(\varepsilon'_{\max}-\varepsilon_\infty)/2U\varepsilon''_1. \tag{11}$$

The calculations give: for $T_1 = 173$°K, $\tau = 2.4\times10^{-4}$ sec; for $T_1 = 200$°K, $\tau_1 = 0.4\times10^{-6}$ sec; the coefficient of the exponential in the expression $\tau = C\exp(U/kT)$ is 10^{-12} to 10^{-13} sec. At room temperature ($T = 300$°K), τ is of order 10^{-8} sec; therefore in a frequency range near 10^8 cps, there should occur a diminution of ϵ' and a frequency maximum of tan δ, in agreement with experimental data. The magnitude of the relaxation polarization is determined[1,3] by the expression $n'q^2x^2/12kT$, where n' is the number of weakly bound ions per cm^3 of the dielectric, q is the ionic charge and x is the distance between neighboring local minima of potential energy of a weakly bound ion. It is easy to see that the following relation holds:

$$\frac{n'q^2x^2}{12kT} = \frac{4\pi(\varepsilon_0-\varepsilon_\infty)}{[4\pi+\beta_1(\varepsilon_{01}-1)][4\pi+\beta_2(\varepsilon_\infty-1)]}, \tag{12}$$

where β_2 is the coefficient of proportionality between the ordinary elastic polarization (due to ionic and electronic displacement) and its contribution to the mean local field. The coefficient β_2 can be estimated by means of the well-known structural internal-field coefficients for a perovskite-type lattice,[3,4] if one assumes that the presence of lattice defects does not appreciably change the internal field produced by ordinary elastic polarization. Such a calculation, with consideration only of the polarization due to electronic displacement, gives $\beta_2 \approx 0.9(4\pi/3)$. An estimate of β_2 can be made by another method, as was done in Ref. 1; according to such an estimate, $\beta_2 \approx 5$. Finally, β_2 can also be found by drawing on additional experimental data. However, the precision of the last estimate is still poorer than that of the first two. On setting $\beta_1 = 0$ and $\beta_2 = 0.9(4\pi/3)$, we get (for $T_1 = 173$°, $\epsilon_{01} = 1330$, $\epsilon_\infty = 250$) $n'q^2x^2/12kT \approx 1$. If we furthermore assume that the number of weakly bound ions is close to the number of bismuth ions in the lattice of the solid solution SBT-1, then for 20 mol percent concentration of bismuth titanate, $n' \sim 9\times10^{20}$ cm^{-3}. There is reason to suppose that the weakly bound ions are the titanium ions in the distorted oxygen octahedra (cf. above); then $q = 4\times4.8\times10^{-10}$ cgs units. Hence for $T = 173$° we find that the relaxational displacement of the titanium ions is $x \sim 0.3\times10^{-8}$ cm. Passage of the titanium ions over such a comparatively short distance within the oxygen octahedron corresponds, as was to be expected, to a small value of the activation energy, ~ 0.3 ev.

Within the framework of this hypothesis of a transition of weakly bound ions across a potential barrier, it is easy to explain why linearity of the polarization persists even at high fields. The linearity can fail if the intensity of the field acting on the weakly bound ion is of order $E_{cr} \approx 2kT/qx$, since then the work by the field in a displacement x is comparable with the energy of thermal motion. For $q = 4 \times 4.8 \times 10^{-10}$, $x = 0.3 \times 10^{-8}$ cm, and T = 300°K, $E_{cr} = 2 \times 10^6$ volt/cm. Upon going over from local to mean field, on the assumption that $\beta_1 \approx 0$ and $\beta_2 \approx 4\pi/3$, we get $E_{av\,cr} \approx 3\,E_{cr}/(\epsilon_\infty + 2) = 2 \times 10^4$ v/cm, whereas the mean breakdown intensity is about 2×10^5 v/cm, i.e., a departure from linearity must take place only at fields close to the breakdown field. Thus the hypothesis of a transition of weakly bound ions across potential barriers in the disturbed perovskite lattice is in more or less satisfactory agreement with experimental data. Other models fit the experiment less satisfactorily. For example, an anharmonic oscillator model must lead to nonlinear polarization even in weak fields. The hypothesis of resonance of the field oscillations with the optical lattice oscillations, which according to formula (6) should occur at lowered frequencies $\omega \approx \omega_0/\epsilon_0{}^{1/2}$ (dispersion in barium titanate[5]), does not agree with experiment in the present case, in view of the change of the frequency of maximum tan δ upon comparatively slight change of temperature. Further studies of the polarization of SBT-1 should lead to the determination of the distribution function of the relaxation times, and also to a clarification of the temperature dependence of the static dielectric constant ϵ_0 in the low-temperature range; and, in particular, to a clarification of the occurrence of "orientational melting," which occurs in crystals containing dipolar groups.

The very high dielectric constant of the SBT-2 dielectrics, as has already been pointed out, is also due to relaxational polarization, which however, is of different character. The curves of temperature dependence of ϵ' and tan δ have a more complicated character (Fig. 4) than do those for the SBT-1 dielectrics. However, an estimation of the activation energy from the frequency shift of the temperature maximum of tan δ (Fig. 4) likewise gives a small value, 0.2 to 0.4 ev. The nature of the polarization of these dielectrics is subject to further study.

---

[1] G. I. Skanvai and E. N. Matveeva, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 1047 (1956); Soviet Phys. JETP **3**, 905 (1956).

[2] A. I. Avgustinnik and N. S. Antselevich, J. Tech. Phys. (U.S.S.R.) **27**, 973 (1953).

[3] G. I. Skanavi and A. N. Gubkin, J. Exptl. Theoret. Phys. (U.S.S.R.) **28**, 87 (1955), Soviet Phys. JETP **1**, 56 (1955).

[4] G. I. Skanavi, J. Exptl. Theoret. Phys. (U.S.S.R.) **17**, 399 (1947).

[5] V. L. Ginzburg, Usp. Fiz. Nauk **38**, 490 (1949).

Translated by W. F. Brown Jr.
68