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The State of Physicochemical Research on Ferroelectric Films

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The review deals with studies on films of complex oxides with unusual dielectric properties. The principal methods for their preparation are described and studies on thin films of barium titanate and solid solutions based on it are considered in detail: the structures at the atomic and supra-atomic levels, the composition of condensed films, structural defects, properties as a function of structure and composition, etc. Data are presented for other ferroelectric complex oxide films as well as thin ferromagnetic layers. Their possible applications are briefly enumerated.
The bibliography includes 257 references.

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I. INTRODUCTION

The continuous development of engineering requires new materials with specified physicochemical properties. Among the materials supplied by chemical industry to meet the requirements of electronic engineering, substances with unusual electrical and magnetic properties (ferroelectric, piezoelectric, and pyroelectric materials, ferrites, etc.) occupy an important place. In recent years increasing attention has been devoted to a research on films of these materials, which are of both theoretical and practical importance.

The principal advantages of electronic devices containing a thin-layer element is simplicity of the technology of their manufacture, microminiaturisation, rapid action, and reduction of the energy consumed and of the controlling fields. On the other hand, a film constitutes a unique model for the investigation of the nature of spontaneous polarisation, side effects, the influence of structural defects on spontaneous deformation, and lattice dynamics, A thin layer is a convenient object for the investigation of the domain and atomic structures of the ferroelectric material up to the determination of atomic coordinates.

The physicochemical properties of films are determined by their chemical composition and atomic-electronic structure. The composition of thin ferroelectric layers is usually more complex than that of metallic, dielectric, and semiconducting films. In the case of mixed oxides, the system consists of 3, 4, and more components, which significantly complicates the mechanism of structure formation, aggravates the phase and structural non-uniformity of the condensed layers, and gives rise to problem of stoichiometry. As a result of the development of electronic probe methods for the analysis of composition and structure, ways have been outlined for determining the compositions of condensates and for optimising the conditions governing the formation of the crystal structure. The role of defects is being more thoroughly investigated. It has become evident that the imperfection of the structure can obscure the true size effects.

After the discovery of barium titanate as a ferroelectric material in the USSR by Vul and Gol'dman[1] (and independently in the USA and Japan), the science of ferroelectricity began to develop rapidly. The relevant monographs[2-10] cover numerous aspects of ferroelectricity, but, with the exception of comparatively short reviews[11-14], the literature on ferroelectric films contains no systematic accounts of data scattered in journal articles, the number of which has sharply increased in recent years.

This review deals with films of oxide ferroelectric materials, which have been the subject of the vast majority of studies on thin ferroelectric layers. Mixed (binary and ternary) oxides have the advantage over other classes of ferroelectric substances as regards relative structural simplicity and the relative simplicity of the technology required to prepare the relevant devices. Ferroelectric materials of the type of barium titanate (with the perovskite structure) have a particularly simple structure, which makes it possible to interpret their properties on a structural basis, and have found extensive practical applications. The restriction of the scope of the review to a discussion of complex oxide films does not rule out the applicability of the fundamental relations of ferroelectricity in thin layers to other classes of materials exhibiting spontaneous polarisation.

II. METHODS FOR THE PREPARATION OF THE FILMS

The problems of the thin layer begin already in the preparation stage, since the structure, properties, and frequently the very presence of the ferroelectric effect depend decisively on the method of synthesis.

There are many methods for the preparation of thin layers: mechanical grinding, chemical etching, slip casting, various kinds of sedimentation, vacuum condensation, etc. The choice of the method depends on the specific problem. For example, the method of deposition on to a support of a suspension of microcrystallites obtained by grinding the starting material is convenient for the structural analysis of the film by electron diffraction. Grinding, casting, and sedimentation are used for the preparation of thick films. Studies on thin films require methods such as vacuum condensation, etc.

A simple method for reducing the thickness of films is mechanical grinding, but this yields high-quality films with a thickness not less than 50–100 μm. Thinner films (15–20 μm) are prepared by slip casting[15-17]. The slip is prepared from a fine-grained powder synthesised

beforehand and having the specified composition. The main fraction of the powder must consist of particles smaller by a factor of 5–10 than the thickness of the cast film. The composition of the binder is chosen on the basis of the conditions governing the optimal formation of the slip, adequate elasticity, and fluidity. The slip is spread on a cleaned support and after drying the film is sintered. The method requires an apparatus for vacuum treating the slip and is used in the mass production of film devices.

One of the sedimentation methods is cataphoresis[18,19] which involves the deposition of the powder from a suspension and subsequent sintering of the layer. The deposition is sometimes carried out in an electric field[20–23] or with the aid of a centrifuge[24]. Films with thicknesses ranging from 5 μm upwards can be prepared by fusion. The initial material is fused on a platinum foil in a specific atmosphere and spreads on the support with formation of a strong single-crystal film[26]. An unusual method involves evaporation from solution; a thin layer of barium titanate consisting of individual crystallites has been prepared in this way[27].

The decrease in thickness by chemical etching involves treatment of a massive specimen (or a single-crystal plate), subjected to preliminary grinding, with a solvent capable of slow dissolution of the material. Hot orthophosphoric acid is used for barium titanate. The method makes it possible to obtain films with a thickness down to 500 Å, but it is then extremely difficult to achieve a uniform thickness. Such layers are used in electron microscopy[28–30]. Single-crystal films with a thickness of several hundreds of ångströms have been prepared by a suspension method[31], but this procedure cannot yield layers with a smoothly varying thickness. The preparation of vitreous layers in a high-temperature flame has been described[32,33].

Methods involving vacuum condensation on a thoroughly cleaned support have found extensive application in the preparation of ferroelectric films. There is a large literature (monographs, reviews, articles; see for example, Refs. 34–36) on this problem. The thickness of the condensate is varied within wide limits, including monatomic layers.

Depending on the method of sputtering of the initial ferroelectric substance, the following procedures can be distinguished:

1. Thermal sputtering by high-temperature heating using a resistance furnace and electron or laser beams[37–40].

2. Cathodic sputtering in which evaporation is achieved by bombarding the substance with inert gas atoms accelerated by a constant field generated by two electrodes (diode sputtering[41]) and by the fields of radiofrequency (RF-sputtering) or high-frequency (HF-sputtering) generators[42–48,68]. When a gas is added to the inert plasma, reactive sputtering takes place[49,50].

We shall now compare the characteristics of thermal and cathodic sputtering. Films prepared by cathodic sputtering require a smaller amount of the starting material, since the target is used repeatedly. Compared with the thermal method of evaporation, cathodic sputtering of compounds having a complex composition ensures a somewhat better stoichiometric composition. Having established the required atmosphere, the second method makes it easier to obtain, for example, oxide films free from an oxygen deficiency. Finally, substances can be subjected to cathodic sputtering over a wide range of temperatures.

On the other hand, the method of thermal sputtering has many undoubted advantages. A simpler equipment is used without the need for a high voltage and exact metering of the gaseous atmosphere, without the difficulties associated with the regulation of the discharge, and without field interference. The rate of condensation is appreciably higher than in cathodic sputtering. Homogeneous films of complex geometry and with a thickness varying in accordance with a specific law are more readily obtained. The thickness of the films is more easily regulated and reproducibility and continuous process control can be more readily achieved. It is significant that thermal evaporation yields purer films compared with cathodic sputtering, in which the rate of adsorption of residual gases may exceed the rate of adsorption of the material condensed. Thus the choice of the method of vacuum condensation depends on the specific material, the specific properties of the films, and technical feasibility.

In the thermal evaporation of ferroelectric materials of complex composition, the so called method of "discrete" evaporation, sometimes referred to as the "instantaneous", "explosive", or "grain-by-grain" method, is most common. It was first used to prepare brass films[51] and was then extended to many materials, including complex oxides with a perovskite structure[52].

The essential feature of the method is that the substance is supplied to the evaporator in small discrete doses. Because of its low heat capacity, each dose vaporises fairly rapidly, creating a vapour with a nearly stoichiometric composition. The condensation of this vapour on the support should give a stoichiometric composition. Under specific condensation conditions, there are additional parameters influencing the composition. For this reason, a modification of the method is used (involving a change in the form of the evaporator, variation of the rate of supply of the material, variation of the composition of the starting material, the introduction of oxygen into the growing film, etc.[39,53,54]).

Compared with other procedures for the preparation of thin films, the vacuum condensation methods have advantages, such as the possibility of smooth control of the thickness (which can reach that of a monatomic layer) and other characteristics of the film by changing the type of support, its temperature, the rate of deposition, etc. The methods of vacuum condensation have been applied on a technological scale and can be used in mass production. A common disadvantage of these methods involves the problem of stoichiometry and structural ordering, which arise from the non-equilibrium conditions in the condensation process.

On the other hand, vacuum condensates have a structure which frequently cannot be generated by other methods (ultrasmall ordered regions with strong disorientation, saturation by defects). This makes it possible to use such films as model systems for the investigation of the influence of the degree of order, the proportion of defects, and other factors on the ferroelectric properties of the substance.

III. THIN BARIUM TITANATE FILMS

1. Atomic and Supra-atomic Structures

Films prepared by methods which do not involve the cleavage of the starting material to the atomic-molecular level (as in vacuum condensation) do not exhibit appreciable changes in atomic structure within the framework of

the structural motif. They can be single crystals, can be obtained by chemical etching of crystals, or by the fusion method, or they can have a polycrystalline structure if they are prepared, for example, by sedimentation methods. While it is evident that the perovskite motif is retained in such barium titanate layers, the problem of spontaneous deformation (c/a) in the thin film is not so clear. It is known[55] that low-temperature synthesis of $BaTiO_3$ leads to a cubic cell ($c/a = 1.00$) and not to a tetragonal cell. The grain dimensions then do not exceed 0.1 μm,[39,56] but suppression of spontaneous deformation is not attributed to the small size of the structural elements but to structural defects in the substance: lattice vacancies[55] and layers of the hexagonal phase[39].

On the other hand, the decrease of the normal spontaneous deformation in particles having a diameter less than 1 μm has been explained[57] by a kind of domain configuration of such very small grains. In the same study an anomaly was observed in the spontaneous deformation in a surface layer 100 Å thick, where c/a exceeded the normal value for barium titanate. This anomaly persists up to 600°C. A similar effect has been described in a study[58] where the tetragonal structure of the surface layer did not disappear up to 430°C. This situation was accounted for by the presence of a thin layer of space charge[59]. Another interpretation[60] involves a change in the composition of the atomic layers near the surface, which becomes close to that of TiO_2 in consequence of the opposed shifts of the Ti and O atoms. However, it remains obscure why the increase of c/a in the thin layer is not manifested in small $BaTiO_3$ crystals, where the role of the surface layer should be considerable.

Electron microscope and electron microdiffraction studies on thin (about 500 Å) barium titanate films[28,29,61] failed to reveal anomalies in c/a or significant deviations from the positions of the atoms in the lattice relative to massive material. This can indicate either errors in the earlier experiments[57] owing to the inadequate resolution of the electron diffraction pattern, as suggested by Tanaka and Honjo[28], or an effect operating in a layer several ängströms thick. On the other hand, appreciable structural changes in the surface layer may be caused by the applied electric field owing to the non-linear distribution of potential[62]. The layer of inhomogeneous deformation caused by the increase of the parameter c and the decrease of a expands with increase of field strength. This fact can explain the contradictions between electrophysical and structural studies (the former revealed anomalies in the surface layer and the latter did not) and also between the data of different workers concerning the thickness of the anomalous layer.

In contrast to the group of studies discussed above, investigation of the structure of vacuum condensates revealed the possibility, in principle, of a dependence of their structure on the conditions of synthesis. Depending on the type and temperature of the support, the rate of condensation, and the stoichiometry, different degrees of ordering, and different types of variation of the size, shape, and orientation of the grains are obtained[38,43,52,63-67,69-73]. In condensation on a cold (t_{room}) support, a disordered structure arises in the $BaTiO_3$ film and the diffraction lines on the X-ray and electron diffraction patterns are diffuse. The nature of the structure of such a film remained obscure for a long time; it was not clear whether it is a result of random shifts of the atoms from their normal positions within the limits of each unit cell (intrinsically amorphous state) or whether it is a normal atomic configuration within the limits of several unit cells with distortion of long-range order (a highly dispersed state). A direct study of the structure by the radial distribution method in combination with high-resolution electron transmission microscopy[74,75] established that the film consists of disoriented regions whose size amounts to several tens of ängströms. The perovskite motif persists within each region, but the interatomic distances deviate somewhat (up to 5%) from their values in the crystalline film as the coordination sphere increases (Fig. 1). The structure of amorphous films with an excess of barium is appreciably different[76].

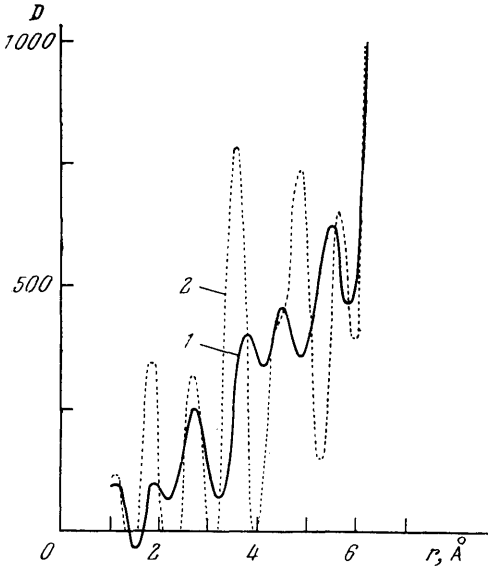


Figure 1. Atomic radial distribution functions D in disordered (curve *1*) and crystalline (curve *2*) barium titanate condensates[74,75].

Structural ordering leading to crystallisation is mainly initiated by the action of heat on the condensate, which the latter can experience during film growth or subsequently. The nature of the crystallisation is different in the two instances and different temperatures are required for the same degree of crystallisation: during subsequent annealing, the temperature must be higher by several hundreds of degrees than the temperature of the support during condensation[38,74,76]. The formation of the structure of the $BaTiO_3$ film on a heated support has been studied by many workers[52,63,65,74,77,78]. At a certain temperature of the support (130–500°C), which depends on its type, the rate of condensation, and the residual atmosphere, crystallites, usually rectangular in shape, begin to develop in the disordered matrix. With increase of temperature, the crystallites grow, filling the matrix, and lose their crystallographic outline in the plane of the film. The orientation of these formations on supports made of ionic crystals is as a rule $\langle 100\rangle \| \langle 100\rangle$. {111} twins on an LiF support[79] and the $\langle 111\rangle \| \langle 111\rangle$ orientation on a platinum foil[18] have also been noted. In crystalline regions, the interatomic distances in the pseudocubic approximation are close to those for the massive crystal[74,76,80]. Thus

the condensate obtained on a heated support has a characteristic microstructure: it comprises single crystal regions distributed in a disordered matrix. In many cases the single-crystal "islands" have the same azimuthal orientation, giving rise to an epitaxial effect [52,74,76,77,79] (Fig. 2).

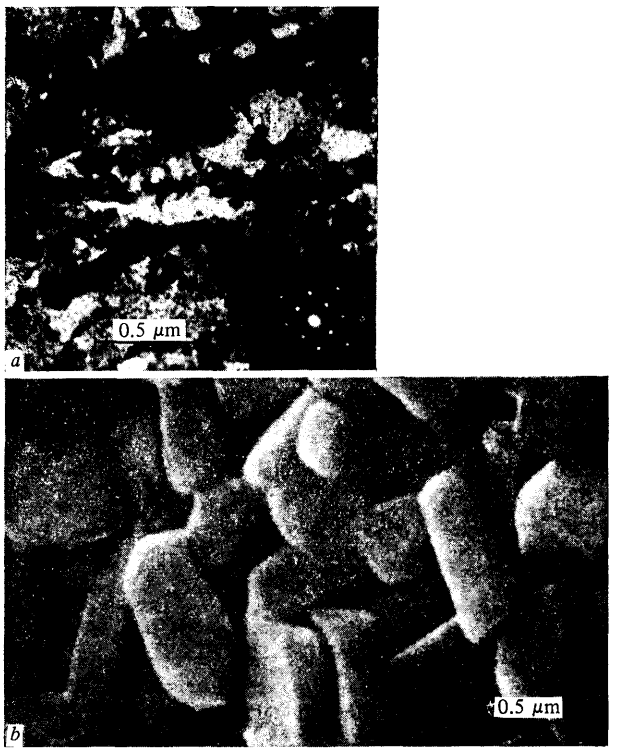


Figure 2. Photomicrographs of a section of barium titanate condensate obtained in different ways: *a*) on a lithium fluoride support heated to 850°C (the diffraction pattern is shown in the lower right-hand corner); *b*) on a cold platinum support with subsequent annealing at 1300°C for 2 h. [74,80]

The causes of the partial retention of disorder in the matrix lie in the considerable proportion of defects in the condensate which are not eliminated by heating. The defects are due primarily to the non-stoichiometry of the film, admixtures of the evaporator material, and other factors [39,74]. Some of the defects serve as centres for the formation of sections with a random orientation.

Heat treatment (starting from $t = 500-1000$°C [38,64,74,81]) of the condensates obtained on a cold support ensures more homogeneous crystallisation, which is revealed by X-ray diffraction. Annealing at 1200–1400°C tends to order the structure, promoting the transition from the cubic to the tetragonal modification and the growth of grains, the size of which can reach between a few tenths of a micrometre to tens and hundreds of micrometres depending on the thickness of the film [39,74,78,82,83] (Fig. 2). The negative influence of high-temperature annealing consists in the growth of crystals of an impurity, which is present in the matrix in a finely dispersed state after condensation [74,84], and also in the formation of cavities between the crystallites in consequence of intense coalesconce processes [64,74,81].

The condensates obtained have a polycrystalline or orientated structure with the direction of texture <100> or <111>. [18,38,39,46,83,85]

The high degree of order does not always guarantee the occurrence of spontaneous deformation in the condensate. In many instances [38,39,86,41,47] the formation of a cubic and not a tetragonal phase at room temperature has been claimed. The transition from the disordered state to a tetragonal structure probably proceeds via the cubic modification. In massive barium titanate, the conversion of the cubic cell into the tetragonal cell occurs at 800° to 1050°C, [39,55,74] while in thin condensed films the transition is delayed, so that $c/a = 1.00$ in some regions of the film even after annealing at 1200–1300°C. [38,41] The quenching of the high-temperature cubic phase in the films can be explained by the appreciable degree of supercooling in the condensation process [84,86,87]. The degree of spontaneous deformation in thin layers is as a rule close to the normal value (~1%), [38,39,41,65,88] although the possibility of the variation of c/a in some cases is not ruled out [83].

The absolute values of the unit cell parameters in the films are usually close to the parameters of the massive material in the pseudocubic approximation. At room temperature, $a = 4.01 \pm 0.02$ Å, [41,88] 4.000–4.030 Å, [39] and $3.99-4.02 \pm 0.01$ Å. [74] An increase of the parameter by up to 2% after condensation on a support at $t < 900$°C has been noted [41] (Fig. 3).

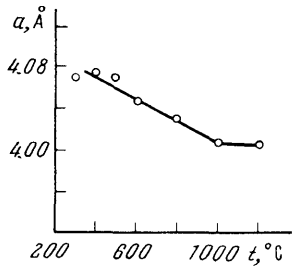


Figure 3. Variation of the unit cell parameter a (in the pseudocubic approximation) of barium titanate films with the temperature of the support t (according to Shintani and Tada's data [41]).

On the whole, one must emphasise that the inadequate resolution of the X-ray diffraction patterns of the condensates preclude a rigorous analysis of the multiplicity of the lines and accurate measurements of the parameters. It is therefore possible that fine structural effects are undetected.

2. Composition

The problem of the composition, which is particularly important for condensed films, did not receive adequate attention for a long time. There is reason to believe, for example, that the stoichiometry of the thin layers obtained in the frequently quoted investigations [89,90] was appreciably

distorted. The suppression of the ferroelectric effect in consequence of the imperfection of the composition and structure of the condensates masks size phenomena. The gap in studies on the compositions of thin barium titanate layers was probably due to the lack of a suitable measuring technique.

In recent years, following the development of electronic probe analysis, a wide variety of X-ray microspectroscopic studies on thin condensates have become possible (the study of the local and total composition, of the distribution of elements, of the thickness, etc.). Methods have been developed for the absolute determination of the stoichiometry in terms of the concentrations of the individual elements of the film [91,92] as well as simpler methods in which the composition of the film is compared with a standard using the ratio of the intensities of the spectral lines [66,93]. It is convenient to employ for $BaTiO_3$ the ratio of the Ba L_α and Ti K_α lines. The standard value is $I_{Ba\,L_\alpha}/I_{Ti\,K_\alpha} = 0.83 \pm 0.05$ for an accelerating potential of 20 kV. [66] The thickness of the layer is determined at the same time from the intensity of the spectral lines of the constituent elements of the film or the support [93,96].

The stoichiometry of the condensates depends on the composition of the molecular vapour, the rate of condensation, the type and temperature of the support, the residual atmosphere, and other parameters. Although the mechanism of evaporation has not been completely elucidated, mass-spectrometric data [82,99] and other considerations [66] indicate a complex composition of the vapour, which contains, together with $BaTiO_3$ "molecules", also BaO, TiO_2, and reduced "fragments", down to metal ions (Tables 1 and 2). Naturally, the complex composition of the vapour phase must have a significant influence on the stoichiometry of the barium titanate condensates. Indeed, there is evidence for the presence of an excess of barium oxide [39,88] in condensed films of the higher oxides $BaO.nTiO_2$ ($n = 2-4$), Ba_2TiO_4, and $BaWO_4$. [38,64,97] The non-stoichiometry of the $BaTiO_3$ condensates prepared by discrete evaporation has been investigated in detail [66,74,98].

Table 1. Composition of the barium titanate vapour under "stationary" conditions* determined mass-spectrometrically (according to the data of Verbitskaya et al. [32]).

Evaporation temp., °C	Material of evaporator	Composition	
		effusion chamber	open surface
2200	Tungsten cell	BaO^+, TiO_2^+, TiO^+, WO_2^+, Ba^+, $BaTiO_3^+$	—
1820	Tungsten cell and strip	BaO^+, TiO_2^+, TiO^+, WO_2^+, Ba^{+2}	BaO^+, TiO_2^+, TiO^+, Ba^+
1980	Iridium strip	—	BaO^+, TiO_2^+, TiO^+, Ba^+

*Under "pulse" (discrete) evaporation conditions, the $BaTiO_3^+$ concentration increases by a factor of 10.

Regardless of the condensation parameters, the films contain different amounts of excess barium ($I_{Ba\,L_\alpha}/I_{Ti\,K_\alpha} > 0.8$), which has an unfavourable influence on the microstructure, being segregated in the form of droplike inclusions. When material with an excess of titanium introduced beforehand is evaporated [53], oxides with a high titanium content are distributed in the matrix without hindering the growth of the perovskite $BaTiO_3$ phase. This can be explained by the crystallisation of $BaTiO_3$ over a wide range of existence, according to the $BaO-TiO_2$ phase diagram [100].

Table 2. Mass-spectrometric composition of the vapour of barium titanate evaporated by the discrete method (according to Nurriddinov's data [99] and the studies quoted in his paper).

Ion	Ba^+	BaO^+	TiO^+	TiO_2^+	$BaTiO_2^+$	$BaTiO_3^+$	WO_3^+	WO_2^+
Relative intensity	0.8	1.0	0.3	0.1	0.06	0.1	0.1	0.08

The favourable role of the excess titanium had been noted earlier [38,101], albeit without any explanation of its causes, for films obtained by evaporation from individual BaO and TiO_2 sources as well as by Feldman's method [37,102]. Films with an excess of titanium ($I_{Ba\,L_\alpha}/I_{Ti\,K_\alpha} = 0.3$ to 0.8) have a structure fairly close to ideality and exhibit ferroelectric properties. Impurities can be identified after high-temperature annealing. As a result of local fluctuations, BaO, Ba_2TiO_4, $BaTi_2O_5$, $BaTi_3O_7$, $BaTi_4O_9$, and sometimes an impurity from the evaporator material have been detected in $BaTiO_3$ condensates. General analysis of the problem of the stoichiometry of $BaTiO_3$ condensates [98] has shown that it is apparently extremely difficult to obtain a rigorously stoichiometric composition.

In addition to the deviation from the stoichiometric proportions of barium and titanium, a deficiency of oxygen is frequently observed in the films, oxygen being lost partly on evaporation of the initial powder and partly on condensation, particularly on a hot support. As a result of the loss of oxygen, some of the Ti^{4+} species are reduced with formation of "defect electrons" and an increase of electronic conductivity. The oxygen deficiency can be eliminated by annealing the film in air or in oxygen at temperatures up to 500°C.

3. Structural Defects

The films, particularly those obtained by condensation, contain an appreciable amount of structural defects. An attempt to give a systematic account of the lattice defects in barium titanate vacuum condensates has been made [74].

Point, linear, and three-dimensional defects are formed during preparation. The first type includes (a) atoms displaced from normal positions and "frozen" following condensation on a cold support, (b) impurity atoms, including "excess" structural atoms present due to non-stoichiometry (local X-ray spectroscopic analysis has revealed between 0.1 and 1 wt.% of the evaporator material), and (c) oxygen vacancies formed under reducing condensation conditions. Other types of defects include the boundaries between the crystallites and the disordered matrix and between the grains as well as microscopic cracks arising in consequence of the relaxation of microstresses as well as cavities produced by coalescence processes.

Table 3. Certain ferroelectric parameters of barium titanate films*.

Method of preparation	Structure	d, μm	ϵ	tan δ	f, Hz	P_s, μC cm^{-2}	E_c	E'	References
Melt	Single crystal	20	4000—6000		50	—	—	—	26
»	»	2—100	100—1000	—	—	2, 2, 5	—	—	121
Etching	»	1—100	600—5000 (at 125°C)		2—200·10^3	—	—	—	107
»	»	3.5—97	—	—	—	5—25	10	—	108
Sedimentation followed by annealing	»	6.7—38.5	500—2000	—	10^3	1—4.5	—	—	18
Electrophoresis	Polycrystalline	0.5—180	⩽820	0.01	—	—	—	—	109
Vacuum condensation	»	2.7	50—1200	—	—	—	7,5	100	78
»	»	10	⩾100	—	—	—	2	—	110
»	»	1.5	300	0.1—0.2	—	0.5—1	—	—	81, 97
»	»	5—7	1100	0.02—0.03	—	—	—	—	82
»	»	0.1—1	20—1330	0.04—0.26	10^3	—	—	10^2—10^3	38
»	Textured	<1	1580	0.04	—	10	100	—	45
»	Polycrystalline, textured	1—12	400—1200	0.02—0.05	10^3	1—14	—	5·10^2—10^3	83
»	Polycrystalline,	0.08—2	28—270	—	1.5·10^6	5.4—6.4	20	100	111, 88, 112
»	Textured	⩾1	—	—		several units	60—80	—	85
»	Polycrystalline, textured	0.5—10	200—600	—	—	9—16	20—40	—	39
»	ditto	0.8—1.2	20—130	0.05—0.15	10^3	—	—	—	46
»	Polycrystalline	2	1700	0.018	10^3	0.2	—	—	41
»	»	0.2—1.25	110—215	0.02—0.05	10^3	—	—	>100	50, 113
»	»	—	150—1500	0.02—0.5	10^3—10^6	—	—	—	114
»	»	0.05—1	400—1500	—	—	—	—	—	115
»	»	3—10	400—1200	0.02—0.05	2·10^3	8—12	—	—	116
»	Polycrystalline, textured	0.5—10	10—2000	—	—	—	—	—	44
»	»	0.2—1	50—350	0.02—0.08	10^3	—	—	>100	47
»	»	0.5	300	0.5	10^3	—	—	—	66
»	»	0.3	1200	0.4	10^3	9	—	—	74
»	»	0.01—0.5	30—1000	0.4—0.5	10^3—10^4	2—10	—	—	117
»	»	0.1—0.35	176—1020	0.05—0.12	10^3	—	—	5·10^2	40
»	»	1—4	100—3000	⩽0.1	—	—	—	—	223, 224
»	Textured	2.5	450 (t=120° C)	⩽0.15	10^9	7—8	20—40	—	225

*d = thickness, ϵ = dielectric constant at room temperature, tan δ = dielectric losses at room temperature, f = frequency, P_s = spontaneous polarisation at room temperature, E_c = coercive field, and E' = dielectric strength.

Structural defects impair and in many cases suppress the ferroelectric properties of the thin layer, the mechanisms of the influence of the defects being various. Presumably the inhibition of the transition from the cubic to the tetragonal structure of the condensate[86] is caused particularly by defects of the point type. There is apparently an analogy between the cubic phase of the films and the radiation-induced cubic modification of massive barium titanate, arising after irradiation with neutrons above the threshold dose of about 10^{18} neutrons cm^{-1}.[103-106] This phase does not exhibit a low-temperature transition to the polarised state and probably lacks ferroelectric properties[103]. The cause of the transition to the cubic phase and of the stabilisation of the latter is believed to be the point defects formed after mixing the atoms. Only prolonged annealing at 1100—1200°C restores the tetragonal structure of the material[105]. Under these conditions, some of the defects are not annealed, which is indicated by an increase in the lattice parameters. Presumably similar processes occur also in condensates.

4. Ferroelectric Properties

The degrees of spontaneous polarisation, dielectric constants and losses, coercive fields, and other ferroelectric parameters of the barium titanate films, based on the data of different investigators, are presented in Table 3. The scatter of the results can be explained by the very great sensitivity of the properties of the thin layer to its previous history (the technology of the preparation and attachment of the electrodes, the electrode material, and the conditions of the measurements). It is necessary to distinguish clearly technological factors, which determine the proportion of structural defects in the films, from size effects.

The influence of structural defects. The "impairment" of the ferroelectric properties of the thin layer compared with the initial barium titanate (the decrease in the degree of spontaneous polarisation, the increase of the coercive field and the dielectric losses, the blurring of the phase transition, etc.) are due primarily to the "dilution" of the ferroelectric phase by regions which are incapable or only partly capable of transpolarisation—the regions of the lattice with zero spontaneous deformation, non-stoichiometric phases, and extraneous inclusions[74,86,98,108].

The dielectric constants of the films depend significantly on relaxation polarisation processes of different types and on the surface states[117,118]. Monomolecular gaseous and organic films on the surface of a ferroelectric material form surface layers with unstable characteristics. The removal of these layers before the deposition of electrodes ensures an adequate reproducibility of the properties[107]. The role of the relaxation mechanisms is manifested in the low frequency dispersion of ϵ and tan δ characteristic of condensates[38,40,44,78,89,118]. The decrease of the dielectric constant and dielectric losses with increase of frequency may be considerable (Fig. 4).

The nature of the ferroelectric phase transition in a thin layer, particularly a condensed layer, is not quite so marked as in massive $BaTiO_3$. The degree of blurring of the transition is determined by heterophase fluctuations in composition (for condensates) or other fluctuations. However, with the exception of cases where a solid solution

based on $BaTiO_3$ is formed in the condensate, the Curie temperature T_C (120°C) is maintained to within 5 to 10 K.[97,102,107,116,117] This fact indicates the existence in the condensates, in addition to the defective regions, of highly ordered regions with spontaneous nearly normal deformation ($c/a = 1.01$). Thus, in contrast to radiation-induced damage, the structural defects are not distributed homogeneously in the condensates. This factor can in fact explain the different types of behaviour of T_C in the films and in irradiated ferroelectric materials. The defects in the condensates influence the degree of blurring of the phase transition, without altering T_C significantly; on the other hand, radiation damages each cell, causing a decrease of c/a and an appreciable shift of T_C towards lower temperatures.

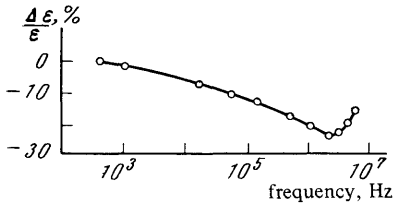


Figure 4. Variation of the dielectric constant of the $BaTiO_3$ condensate with frequency[44].

Size effects in films. The results of studies on the ferroelectric parameters of thin films, which may be treated as the manifestation of dimensional effects, although in many instances technological factors cannot apparently be fully ignored, are considered below.

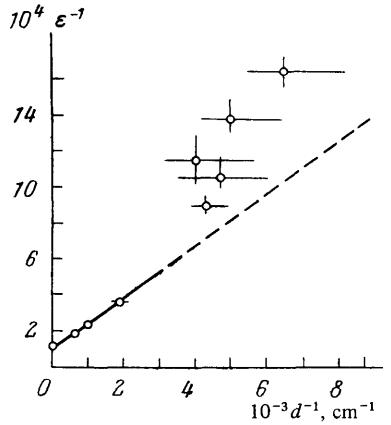


Figure 5. Variation of $1/\epsilon$ for single-crystal $BaTiO_3$ films obtained by etching with $1/d$ (according to Makarov's data[107]).

The dependence of the dielectric constant on the thickness of single crystal films obtained by the attenuation method has been studied in a series of investigations[25,26,107,119-122]. At an early stage it was concluded that ϵ increases as the thickness of the layer is reduced[26], but subsequent studies by the same and other investigators showed that the variation of ϵ with d is linear down to $d \simeq 3.5$ μm, a deviation from the relation being observed below this limit[107,119,123,124] (Fig. 5). The decrease of ϵ is caused by the decrease of the effective Curie–Weiss temperature[107]. The Curie–Weiss constant is independent of the thickness of the crystal in the range $1 \geqslant d \geqslant 4000$ μm.

The coercive field in the tetragonal phase increases with decrease of d,[25,122] but in low-temperature modifications the increase is not quite so great. An increase of P_S in a thin layer (up to 6 μm) relative to a thicker film has been observed[121]. However, later the same authors concluded[25,119] that the dependence of P_S on thickness is weak for $d \geqslant 1$ μm. According to these data, the tetragonal structure and transpolarisation persist down to 1 μm in accessible fields. The absolute degree of spontaneous polarisation is appreciably reduced compared with massive $BaTiO_3$. The decrease of P_S in films prepared by deposition followed by sintering has also been noted by other investigators[18], although in this case the defects probably played an appreciable role. In layers with $d \leqslant 10$ μm, obtained by etching, a monotonic decrease of the degree of spontaneous polarisation with thickness was demonstrated[108].

The smoothing of the $\epsilon(t)$ relation with decrease of thickness has been noted[121]. For $d = 1$ μm, the maximum in the $\epsilon(t)$ relation at 120°C disappears, but reappears in a stronger field, albeit in a diffuse form. The retention of $T_C \simeq 120$°C for $d \geqslant 1$ μm is significant[120].

The smoothing of the maximum in the $\epsilon(t)$ relation near 120°C with decrease of d has been noted[25]. A similar effect has also been observed in thinner layers prepared by condensation[117] (Fig. 6). For a $BaTiO_3$ vacuum condensate with a thickness of 100 ± 20 Å, the $\epsilon(t)$ maximum in the region of 120°C is completely smoothed out, while both low-temperature maxima are retained.

It must be emphasised that the increased proportion of defects in condensed layers does not rule out the possibility of using them for the investigation of size effects, for example, the dependence of dielectric parameters on thickness. A set of films with different thicknesses, obtained under similar condensation conditions (identical proportions of defects), made it possible to determine the $P_S(d)$ relation in the range $100 \leqslant d \leqslant 1400$ Å (Fig. 7).[117] At room temperature, P_S decreases with thickness from about 10 μc cm^{-2} ($d \geqslant 1400$ Å) to approximately zero for $d \simeq 100$ Å. The thinnest ferroelectric layers (100–200 Å) have apparently been obtained in a study by the present author and Sevost'yanov[117].

5. The Theory of Size Effects in $BaTiO_3$

The decrease in the size of an object below a certain limit leads to a change in its properties (the size effect). The critical size is different for different properties.

The theory of the size effect in ferroelectric materials is based on thermodynamic and microscopic concepts, which permit a qualitative (at best semiquantitative) description of the critical phenomenon. For ferroelectric materials, the concept of the critical size is related to parameters such as spontaneous induction D_S (polarisation P_S) and deformation, the Curie temperature T_C, the dielectric constant ϵ, the domain structure, etc.

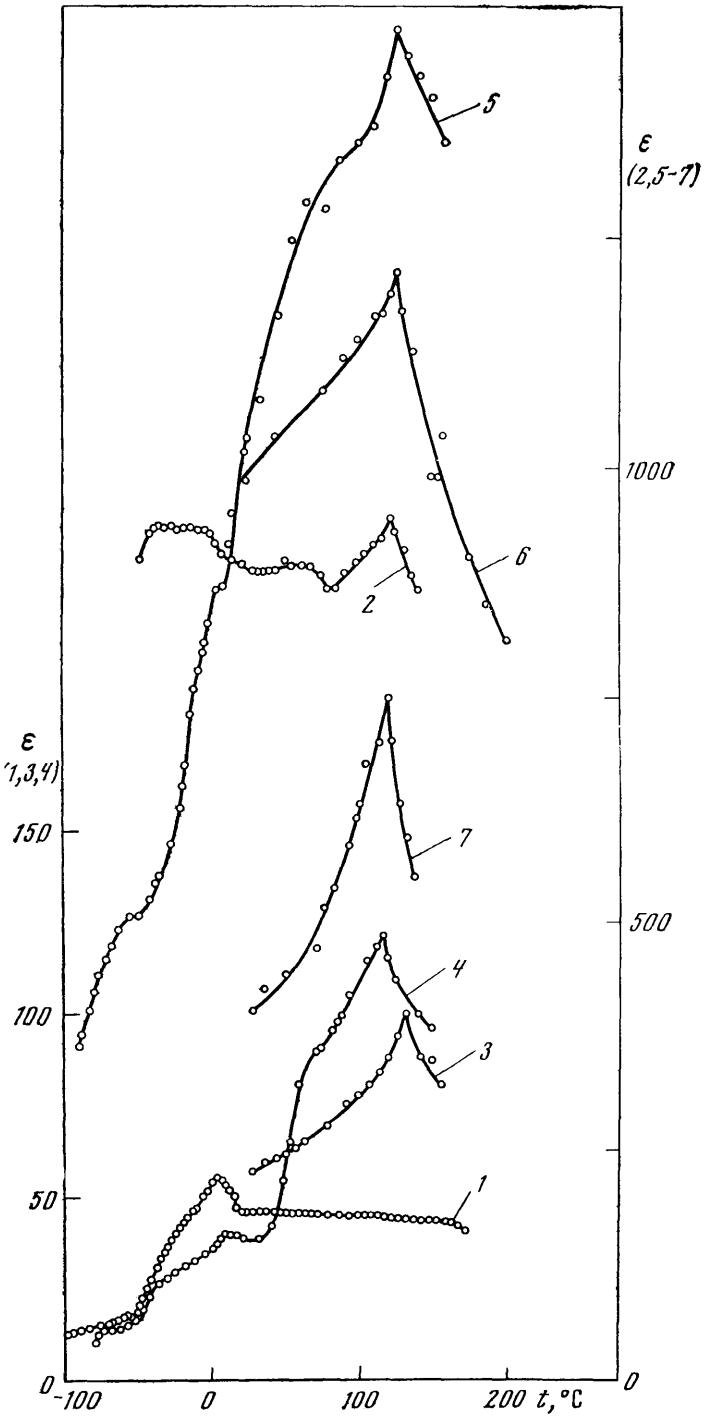


Figure 6. Temperature variation of ϵ for barium titanate condensates with different thicknesses (Å): 1) 100; 2) 230; 3) 430; 4) 450; 5) 680; 6) 800; 7) 5000 (according to Tomashpol'skii and Sevost'yanov's data [117]).

In depolarisation field models [125-132], the presence of an incompletely shielded depolarisation field E_{det}, directed in opposition to P_S, is postulated in a thin C-domain crystal. Ivanchik [125] took into account the mechanism of shielding by free carriers alone. At equilibrium, characterised by a minimum in the free energy F, the latter is expanded as a series (the usual procedure in a formal thermodynamic treatment) in terms of the spontaneous induction D_S (polarisation) with retention of higher terms and differentiation with respect to the expansion parameter.

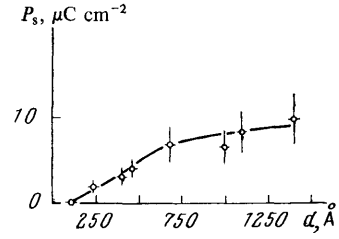


Figure 7. Experimental variation of P_S with d for barium titanate condensates (according to Tomashpol'skii and Sevost'yanov's data [117]).

The assumption of partial conductivity of the crystal makes it possible to express the electric field E in terms of the charge density, which is in its turn a function of D_S. Thus a closed equation, the solution of which determines the dependence of the ferroelectric parameters on the thickness of the crystals d, is obtained for D_S (or P_S). Apart from the semiconductor shielding mechanism, others, for example, mechanisms associated with structural defects, have also been proposed [126].

Ivanchik's ideas [125] were subsequently extended to a ferroelectric–electrode system with a distributed space charge [127-131], more detailed account being taken of the influence of the electrical contact conditions: the material of the contacts and methods for achieving them.

The depolarisation field model yields a relation between P_S, T_C, and d. An estimate of the critical thickness (corresponding to the complete disappearance of the effect) leads to 200–500 Å for barium titanate [125,132]. This approach explains qualitatively the experimentally observed decrease with thickness of P_S and the pyrocoefficient γ and the blurring of the phase transition. However, the model is not free from disadvantages, which hinder a quantitative interpretation of experimental data. The assumption of semiconducting properties implies the presence in the ferroelectric of a definite number of free carriers, which contribute to the shielding E_{dep} and promote its "dissipation". It has been noted [133] that a prolonged action of E_{dep} in conducting crystals is unlikely and its numerical value is "the subject of a major controversy" [130]. Furthermore, the theoretical conclusion that T_C is appreciably displaced towards lower temperatures with decrease of d has not been confirmed experimentally for $BaTiO_3$ down to thicknesses of about 200 Å. [117,119] No account is taken in the model of surface states [134], which can have an appreciable influence on the redistribution of polarisation charges owing to their partial or complete compensation on the surface [135]. Finally, the model is valid only for the C-domain state, whereas in reality one encounters, apart from the C-domain configurations [136,137], also A-domain thin layers [29,111,119], for which the influence of E_{dep} is not significant [138].

According to the dynamic model[119,120], in which the lattice vibrations of a ferroelectric plate with a limited thickness d in the z direction are considered under the conditions of a transverse frequency ω_t, the dielectric constant ϵ_z should decrease with decrease of d, while ϵ_x and ϵ_y should remain invariant. T_C does not change significantly.

In a monoaxial ferroelectric ($P_S \| z$), a phase transition would be impossible for a certain thickness. In the case of $BaTiO_3$ the presence of three equally valid directions of P_S should lead to the conversion of the thin layer into the A-domain form and only a weak variation of P_S with thickness. Thus the dynamic model does not predict significant changes of P_S for thin crystals of the $BaTiO_3$ type or a shift of T_C with decrease of film thickness. According to the model, the Curie–Weiss temperature and the dielectric constant decrease for low values of d, while the $\varepsilon(t)$ relation is smoothed out owing to the ϵ_z component. The limitations of the model involve, in particular, the fact that its conclusions are valid only for the thickness range $1 \leq d \leq 300$ μm.[120]

In the electrostatic model of the thin layer of a ferroelectric material[117,139], one considers the dependence on thickness d of fields due to dipoles and charges and the Lorentz (E_{Lor}) and depolarisation (E_{dep}) fields in C- and A-domain films of the barium titanate type. The behaviour of the internal electric fields E_i and of spontaneous polarisation P_S with decrease of d is determined by the relative contributions of the opposed E_{Lor} and E_{dep} fields. The Lorentz field begins to decrease with decrease of the thickness below the critical value, which has been estimated as 300–500 Å, depending on the chosen size of the Lorentz cavity. When $d < 300-500$ Å, the model predicts an appreciable decrease of E_i and P_S. If $E_{dep} = -4\pi P$ (P is the polarisation), i.e. is not shielded, then $P_S \to 0$ when $a = 80-100$ Å for a C-domain film. When E_{dep} is weakened or absent (an A-domain crystal), a low value of P_S persists for $d < 100$ Å. The model does not rule out the occurrence of spontaneous polarisation in layers with a thickness below 1000 Å and yields a $P_S(d)$ relation which can be reconciled with experimental data[117] for a suitable choice of parameters. The inadequate rigour of the criteria governing the choice of the critical thickness makes the model semiquantitative.

A fairly simple model, which explains the anomalies in the ferroelectric properties of thin crystals, is that of the surface layer[57,112,123], based on experimental evidence for its existence. Regardless of their nature, surface layers are considered anomalous from the standpoint of ferroelectric behaviour. A thin crystal is treated as a layer condenser, the internal component of which consists of the "normal" ferroelectric and the outer regions consist of the "anomalous" material (with a low value of ϵ, a high coercive field, etc.)[123,124]. The overall value of ϵ, which decreases with decrease of film thickness for a constant depth of the surface layer, is calculated in terms of this scheme.

The model explains the decrease of ϵ, the smoothing of the $\epsilon(t)$ relation in the region of the phase transition, the increase of the coercive field, and other anomalies in the film. However, one must point out certain experimental data which are difficult to account for within the framework of this model. Kanzig and coworkers[57] suggested that the surface layer model is based on the structural distortions within the cell. On the other hand, electron microscope[28], electron microdiffraction[61,140,141], and X-ray[142] studies failed to reveal such distortions in the crystals (with thicknesses down to 500 Å) and in the surface layer of $BaTiO_3$ with a thickness of hundreds of ängströms. The presence of a strong electric field in the surface layer[62,143,144] should lead to an increase of the concentration of C-domains near the surface. However, as stated above, experimental data indicate a tendency by thin films (where the surface layers should have an appreciable negative volume) towards conversion into the A-domain form[29,111,119]. In the surface layer model, its non-ferroelectric nature (low values of ϵ, high coercive fields, the absence of transpolarisation, etc.) is usually emphasised. Direct observation of the domain structure of $BaTiO_3$ with the aid of a scanning electron microscope[145] indicates a ferroelectric behaviour of the regions near the surface. Finally, the results of different studies concerning the depth of the surface layer h and its dielectric constant ϵ are characteristically contradictory ($h = 0.01$ to 25 μm, $\epsilon = 5-1080$).[59,112,123,124,135,146-152]

Evidently the depth of the surface layer (if it exists) is not a single-valued film parameter, depending on many factors (mechanical treatment, heat treatment, the applied field, irradiation with light, etc.)[3,58,153]. It has been noted correctly[120] that the surface layer model is very flexible, because it operates with a number of adjustable parameters. However, the uncertainty of the parameters introduced precludes the use of the model for a rigorous quantitative comparison with experiment.

The ferroelectric characteristics of thin layers (in particular vacuum condensates) can be calculated using a model the ferroelectric properties of which are determined by the degree of "dilution" of the ferroelectric phase by non-polarised regions, without specifying the nature of the latter: this may be a quenched high-temperature phase, defective regions where there is no transpolarisation, and extraneous impurities. P_S for such a mixture can be calculated within the framework of the electrostatic model from the effective atomic shifts[74,86] and the dielectric constant can be found from the formulae of Grossman and Isard[154].

Thus theoretical analysis explains the dimensional effect in thin ferroelectric layers: the decrease of P_S, ϵ, and γ, the blurring and shift of the phase transition (T_C), and the change in the lattice vibration spectrum.

The theory predicts a critical film thickness, below which $P_S = 0$. The specific form of the relations between the ferroelectric characteristics and the critical size on the one hand and d on the other is a function of a number of parameters (conductivity, electrode material, the surface state, the domain structure, etc.). In the depolarisation field model, the critical thickness is 200–500 Å and in the electrostatic model 80–100 Å (for a C-domain film in the absence of shielding from the depolarisation field).

6. $BaTiO_3$ Films as Models in Studies of the Ferroelectric State

Determination of the critical size of ferroelectric "nuclei". In the model of ferroelectric nuclei[155], it is assumed that small regions of the tetragonal modification arise in the deep paraphase, grow with decrease of temperature to T_C, reaching the critical size, and below T_C are converted into a system of 180-degree domains. Bearing in mind that the cessation of the growth of the "nuclei" before the attainment of the critical size (when the latter exists) owing to restriction by the natural grain boundaries should lead to the suppression of the "normal" ferroelectric behaviour (dimensional effect), an attempt has been made[156] at an experimental

determination of the critical size of the region of the tetragonal phase in barium titanate. Condensed films where there is a possibility of an extensive variation of the grain size, from tens of ängströms to hundreds of micrometres are unique models for such research.

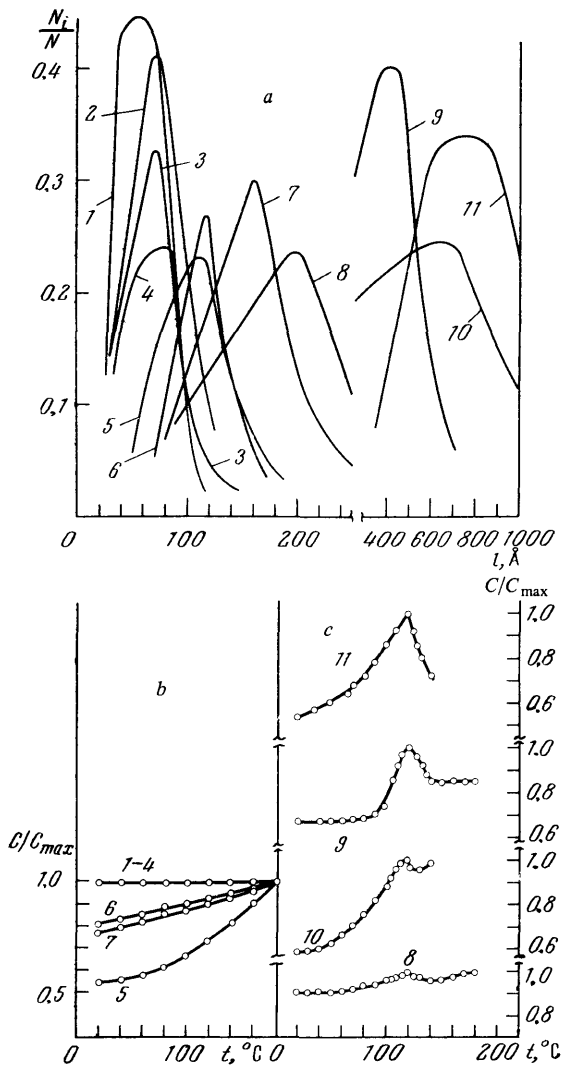


Figure 8. Distribution of grains (N_i/N) with respect to size (*a*) and temperature variation of the relative capacitance C/C_{max} (*b* and *c*) of condensed barium titanate layers (according to Tomashpol'skii and Sevost'yanov's data [156]); the numerals opposite the curves in the lower part of the figure correspond to the numerals in its upper part.

Fig. 8 presents the results of dielectric measurements on films with different average grain sizes, which show that there exists a limiting grain size $l \simeq 180-250$ Å, below which there are no ferroelectric anomalies and which may be compared with the critical "nucleus". The experimental critical size is satisfactorily correlated with the size of the fluctuation regions in the vicinity of T_C, observed by Kanzig [157] and calculated theoretically in a number of investigations [158-161].

Determination of the group velocity of phonons in the ferroelectric mode. The decrease of the dielectric constant has been explained by a change in the bulk-phase vibrations in thin ferroelectric layers [119]. In this approach, the experimental study of the size effect in films makes it possible to determine certain parameters of the dynamic model for those regions of the phonon spectrum where ultrahigh-frequency and neutron spectroscopic methods are ineffective. A high velocity of phonons has been obtained from the dielectric constant of single-crystal barium titanate films: $\sqrt{B} \simeq 10^7$ cm s^{-1} (B is a constant related to long-range forces in the dynamic theory) [107].

IV. FILMS OF SOLID SOLUTIONS BASED ON BARIUM TITANATE

The characteristics of films of the solid solutions Ba(Ti, Sn)O_3 and (Ba, Sr)TiO_3 with a thickness in the range 10–500 μm, obtained by the slip casting method, have been investigated in a number of studies [124,162,174], while others, prepared by the grinding method (30–35 μm thick), by etching (with a thickness from 40 μm upwards), and by cataphoresis (approximately 80 μm thick), have been investigated by Morozov [163], Burfoot and Sensordenker [164], and Yamanaka et al. [165] respectively. For $d \geq 30$ μm, the coefficient of non-linearity, ϵ, and P_S remain high [162,174]. However, for $d < 30$ μm, the coefficient of non-linearity and other parameters decrease. As the thickness is reduced below 500 μm, the controlling potential falls, which makes it possible to employ non-linear film elements based on (Ba, Sr)TiO_3 in semiconductor circuits [124]. The ultrahigh frequency dispersion in the ferroelectric phase and the maintenance of the validity of the Curie–Weiss law in the paraphase have been observed [163]. Certain optical characteristics of thick films with 25% Sr have been published [164].

In the preparation of solid solution vacuum condensates, additional problems associated with stoichiometry arise. The contradictory nature of the data obtained for condensed films is associated primarily with the inadequate control of their composition and structure. Thus, an increase of the dielectric constant with decrease of thickness from 1.6 to 0.1 μm, has been reported [89], the absolute value of ϵ amounting to several thousands. $\epsilon < 50$ has been obtained for similar films in another study [90]. The validity of the results of a particular investigator is difficult to establish, since the composition of the condensate was not followed in either study. (Ba, Sr)TiO_3 films 2–3 μm thick have been obtained [78] by the method of discrete evaporation and $\epsilon(l)$ maxima, displaced towards lower temperatures compared with pure $BaTiO_3$, have been observed. Low-frequency dispersion has been found in the range 10^2-10^6 Hz. $P_S < 1$ μC cm^{-2} has been obtained at room temperature for a $(Ba_{0.95}Sr_{0.05})TiO_3$ film 2.4 μm thick.

(Ba, Sr)TiO_3 vacuum condensates with a thickness less than 1 μm have been obtained and investigated in a series of studies [118,166-168]. The structures and compositions were determined by X-ray diffraction and by local X-ray spectroscopic analysis. In order to correct for the excess barium and strontium, the initial material had a composition with a barium deficiency [53]. The structure of the films was of the perovskite type with parameters close to that of the starting material, provided that the multiplicity of the X-ray lines was disregarded. The ferroelectric behaviour of the solid solution condensates

was confirmed by the dielectric hysteresis [$\epsilon(t)$ peaks], which disappeared at temperatures above those of the phase transitions. As for massive specimens, the $\epsilon(t)$ maxima shifted towards lower temperatures with increase of the strontium content. The limiting thickness of the solid solution film in which transpolarisation was still observed amounted to about 700 Å.

The decisive influence of structural ordering and stoichiometric factors on ferroelectric properties has been demonstrated and it has been shown that the structural defects in the films initiate relaxation processes. Spontaneous polarisation coexists under the conditions with relaxation polarisation, the contribution of which may be fairly high. A characteristic feature of the films is a high value of $\tan\delta$ (amounting to several tenths at low frequencies), low frequency dispersion, and the blurring of phase transitions.

(Ba, Ca)TiO_3, Ba(Ti, Sn)O_3, Ba(Ti, Zr)O_3, and (Ba, La)TiO_3 condensates have been investigated[42,167,169]. After heat treatment, admixtures of TiO_2 and other phases are detected in the films together with the perovskite modification. Following the addition of 14% La or Ca, T_C falls to room temperature. The difference between the values of ϵ for the film and the massive material does not exceed 5% and the dielectric losses amount to 0.01 to 0.03. For (Ba, La)TiO_3 condensates obtained by cathodic sputtering[169], $\epsilon \simeq 200$ (at a frequency of 1.5 kHz) and $\tan\delta \simeq 0.02$ dielectric strength $\simeq 10^5$ V cm^{-1}.

V. OTHER COMPLEX OXIDE FILMS

1. Strontium Titanate ($SrTiO_3$)

The preparation of strontium titanate vacuum condensates among other perovskites materials was reported for the first time by Muller et al.[52] Thin layers obtained by cathodic sputtering were investigated in greater detail by Pennebaker[49], who found that, when this method is used, the properties of the films are influenced mainly by the size of the crystallites and the oxygen pressure. Although many properties of the condensate proved to be similar to those of the starting material, nevertheless ϵ amounted to 65% of the value for massive $SrTiO_3$ and the losses were appreciably higher. The variation of ϵ and $\tan\delta$ with thickness and dielectric strength of 500 kV cm^{-1} have been observed[170] for films obtained by the same method.

The structures and properties of strontium titanate films 0.05–1 μm thick, prepared by the method of discrete evaporation, have been investigated in detail[171-173]. The principal parameter determining the stoichiometry with respect to strontium and titantium is the rate of condensation, which leads to an excess concentration of strontium when it exceeds the optimum value (≤ 1 Å s^{-1}). Condensation on a heated support is responsible for the appreciable losses of oxygen from the film compared with condensates deposited on a cold support. The oxygen deficiency can be partly or completely compensated by subsequent annealing in air or in oxygen.

In the disordered state, the film consists of a collection of arbitrarily oriented regions whose size amounts to several tens of ängströms. Within each region, the perovskite motif is maintained but the interatomic distances are somewhat different from those in the massive crystal. High-temperature treatment results in ordering processes leading to crystallisation. In the crystalline state, the unit cell parameters are close to the initial values (for the massive specimen). At low temperature, the behaviour of the $\epsilon(t)$ relation is different for the disordered and crystalline films. For the former, ϵ falls slowly with decrease of temperature, and for the latter it increases, although more slowly than the value for the initial crystal. At −100°C and a frequency of 1 kHz, $\tan\delta = 0.01-0.001$ in disordered films and the dielectric strength is $\sim 10^6$ V cm^{-1}.

2. Lead Titanate ($PbTiO_3$)

Condensates 0.1–0.3 μm thick have been prepared by the cathodic sputtering method[175]. In order to achieve a stoichiometric composition, the lead content in the target did not exceed 5%. The dielectric constants ϵ of these films amounted to several tens. Films with structures closer to ideality, prepared by the same method, had dielectric constants which depended on the molar ratio Pb : Ti and amounted to about 500 in the optimum case (1 : 1).

3. Lead Zirconate ($PbZrO_3$)

Thick $PbZrO_3$ layers have been prepared by deposition in a constant electric field[22,176]. Their dielectric constants are several times smaller than the values for polycrystalline specimens and the dielectric losses are higher in consequence of the porosity of the layers. A shift of T_C towards higher temperatures has been observed.

4. $(Pb_{0.92}Bi_{0.07}La_{0.01})(Fe_{0.405}Nb_{0.325}Zr_{0.27})O_3$

Films 2–16 μm thick with a perovskite structure and having the above complex composition have been obtained by deposition followed by sintering[177]. For these layers, $\epsilon \simeq 1000$ and $T_C = 150$°C. The degree of spontaneous polarisation amounts to 10–20 μC cm^{-2} and the coercive field is ≥ 15 kV cm^{-1} with a satisfactorily rectangular hysteresis loop. One of the films of this series withstood 2×10^{11} switchings lasting 300 ns at a potential of 20 V.

Studies on films of the same composition, prepared by radiofrequency sputtering, have been reported recently[178]. For films 4.5 μm thick, it has been found that $\epsilon \simeq 1600$, $P_S = 3-15$ μC cm^{-2}, the coercive field is 5–10 kV cm^{-1}, $T_C \simeq 80$°C, and the resistance is $\sim 10^{14}$ Ω cm. The condensates withstood 10^{11} switchings lasting 200–600 ns without appreciable changes in P_S and the coercive field.

5. Calcium Titanate ($CaTiO_3$)

Vacuum condensates 0.1–0.3 μm thick with $\epsilon = 20-60$ have been obtained[179]. Their high dielectric strength (up to 10^7 V cm^{-1}) is striking. The structures and properties of the films, prepared by discrete evaporation, have been studied[180]. The unit cell parameter in the pseudocubic approximation is $a = 3.90 \pm 0.05$ Å, which somewhat exceeds the values for massive $CaTiO_3$ ($a = c = 3.819$ Å and $b = 3.815$ Å); the dielectric constant is 500–700 (for the initial ceramic, $\epsilon = 200$), but the dielectric losses in the films are higher ($\tan\delta = 0.5$ against 0.2 in the massive specimen). The electret properties of ceramic calcium titanate films have been studied[181]. An electric field has not been detected in the films in the presence of an appreciable space charge.

6. Tungsten Trioxide (WO_3)

The microstructure and certain physical properties of WO_3 condensates have been described[182]. The films were deposited *in vacuo* (10^{-5} mmHg) on glass supports. The observed characteristics are complex functions of technological parameters.

7. Lithium Niobate ($LiNbO_3$) and Lithium Tantalate ($LiTaO_3$)

Foster[183] reported studies on lithium niobate films 2–4 μm thick obtained by cathodic sputtering. The condensates proved to be weakly textured, had $\epsilon = 65$ at a frequency of 1 kHz and a piezoelectric coefficient of about 0.08, which is about 50% of the value for a single crystal along the z axis. The preparation of $LiNbO_3$ and $LiTaO_3$ films by high-frequency sputtering has been described[47,184]. The authors observed a deficiency of lithium in the film and enriched the target in lithium for the purpose of compensation. The ferroelectric properties of these condensates are weak: $\epsilon = 80-100$ and $\tan\delta \simeq 0.1$.[47] The elements of the epitaxial growth of $LiNbO_3$ condensates with the (001) orientation, prepared by discrete evaporation on a single crystal layer of silver, have been determined[185]. Attempts have been made to grow single-crystal $LiNbO_3$ films for optical purposes[186].

8. Ferroelectric Niobates

Thin layers having the $KNaNb_2O_6$, $Ba_2NaNb_5O_{15}$, $K_3Li_2Nb_5O_{15}$, and $PbNb_2O_6$ compositions have been obtained by cathodic sputtering on SiO_2 supports coated with gold[187]. The stoichiometry was maintained to within 10–15%. A weak piezoelectric effect was observed in some of the films.

9. Bismuth Titanate ($Bi_4Ti_3O_{12}$)

Epitaxial layers of bismuth titanate have been obtained[188-191]. The condensation temperature was varied from 400° to 700°C and the target consisted of a ceramic with an excess of bismuth to compensate for its losses. The thickness of the films on MgO and platinum supports was 0.2–4.5 μm. The dielectric characteristics, including the degree of spontaneous polarisation, agree well with the values for the massive crystals. Domain boundaries were observed in films 12–32 μm thick[189].

10. Lead Germanate

The discovery of the ferroelectric effect in lead germanate was reported recently[192,193]. The new ferroelectric belongs to the trigonal system, the threefold axis is polar, and $T_C = 170-180$°C. According to the authors[192,193], the formula of the ferroelectric crystal is $5PbO.3GeO_2$, but one cannot rule out a somewhat different composition, namely $3PbO.2GeO_2$.[194,195] Polycrystalline lead germanate films with a thickness <1 μm and having a structure and composition close to those of the initial single crystal have been prepared by discrete evaporation and investigated[196]. An anomaly in the $\epsilon(t)$ relation, corresponding to the phase transition in the massive crystal (T_C), and a dielectric hysteresis loop were observed. The degree of spontaneous polarisation is about 70% of its value for the single crystal.

11. Strontium Tellurate ($SrTeO_3$)

A characteristic feature of this new ferroelectric is that its ferroelectric properties are observed in the temperature range 312–485°C.[197] Films about 0.1 μm thick were obtained by the vacuum evaporation of the comminuted ceramic $SrTeO_3$, for which the temperature range of the polarised state was found to be 325–470°C.[198] Polycrystalline layers can be made even when the support is at room temperature. Heat treatment of the films in air leads to a distinct maximum on the $\epsilon-t$ curve at 470°C, corresponding to T_C for the ceramic. A lower limit of the ferroelectric region was not observed.

12. Antimony Orthoniobate ($SbNbO_4$)

Antimony orthoniobate, a new ferroelectric material, has $T_C = 403$°C and $P_S = 15$ μC cm^{-2} at room temperature, according to Lobachev et al.[199] $SbNbO_4$ vacuum condensates, obtained by discrete evaporation, have a polycrystalline structure[200]. The $\epsilon(t)$ relation has a maximum in the region of 380°C. For the films with the composition closest to stoichiometry, dielectric hysteresis was observed at room temperature; $P_S = 7.4$ μC cm^{-2} and $\tan\delta = 0.1-0.5$.

It has been reported recently[201] that $SbNbO_4$ is an antiferroelectric above 403°C and that the transition to the paraelectric region (T_C) occurs at 600°C.

VI. FERROMAGNETIC VACUUM CONDENSATES

The combination of ferroelectric and ferromagnetic dipoles in a structure of the perovskite type has been achieved in a ceramic consisting of solid solutions of ferroelectric–ferromagnetic systems[202,203], one of the components of which is the $Sr_{0.3}La_{0.7}MnO_3$ solid solution with the magnetic Curie point $T_C^M = 90-120$°C.[204,205]

Condensates of the $BaTiO_3-Sr_{0.3}La_{0.7}MnO_3$ system have been investigated[206]. Films approximately 1000 Å thick with the composition close to $(Ba_{0.9}Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ were prepared by discrete evaporation, varying the composition of the starting material and subjecting the film to heat treatment during and after condensation. The composition and structure were investigated by local X-ray spectroscopic and X-ray diffraction analyses.

Fig. 9 illustrates the temperature variation of the relative dielectric constants ϵ/ϵ_{max} and of the half-widths ΔH of electron spin resonance lines for films of the initial components $BaTiO_3$ and $Sr_{0.3}La_{0.7}MnO_3$ as well as the condensate of the above composition. The $\epsilon/\epsilon_{max}(t)$ maximum, corresponding to the ferroelectric Curie point T_C, is displaced from 120°C for the pure $BaTiO_3$ film towards lower temperatures following the addition of $Sr_{0.3}La_{0.7}MnO_3$. The $\Delta H(t)$ minimum, corresponding to T_C^M (90°C)[207] for the $Sr_{0.3}La_{0.7}MnO_3$ condensate, also moves to the region of lower temperatures. Thus $T_C^M = -120$°C and $T_C^E \leq -130$°C were obtained for the $(Ba_{0.9}.Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ films. Compared with a

ceramic of similar composition and also with films of the initial components, the transitions in the ferromagnetic film are diffuse and occur at lower temperatures, probably owing to fluctuations in composition.

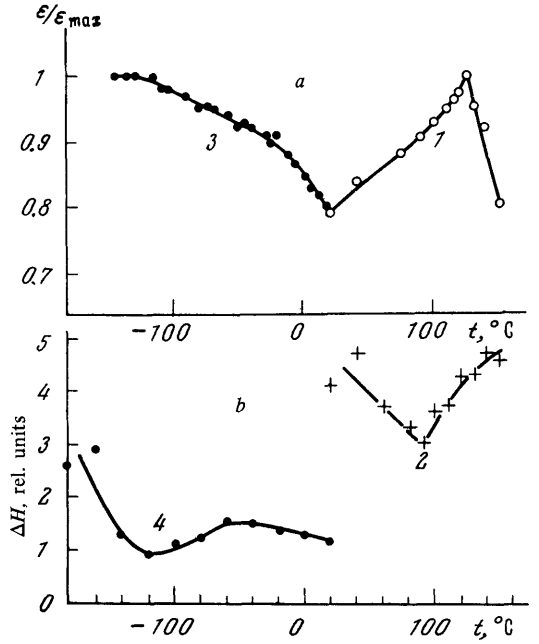


Figure 9. Temperature variation of the relative dielectric constant ϵ/ϵ_{max} (*a*) and electron spin resonance line half-width ΔH for the manganese ion (*b*) in films of the initial components $BaTiO_3$ (curve *1*) and $Sr_{0.3}La_{0.7}MnO_3$ (curve *2*) and the condensate $(Ba_{0.9}Sr_{0.03}La_{0.07})(Ti_{0.9}Mn_{0.1})O_3$ (curves *3* and *4*) [206].

VII. CERTAIN APPLICATIONS OF THIN FERROELECTRIC LAYERS

The need for thin ferroelectric layers in a wide variety of electrical and optical instruments as condensers, pyroelectric detectors, piezoelectric transducers, memory elements, and indicator elements is fairly considerable [13,14]. It has been concluded [208] that one of the important applications of ferroelectric films may be their use as condensers for microwave amplifiers in multimodular systems. The requirement for a high value of ϵ and a low value of $\tan\delta$ at high frequencies is important here. $BaTiO_3$ and $PbTiO_3$ films are therefore less suitable for such purposes than, for example, $Bi_4Ti_3O_{12}$ condensates. The latter ensure a high capacitance (0.02–0.2 μF) and low dielectric losses up to frequencies of about 10^9 Hz. Condensed $SrTiO_3$ films with $\epsilon = 200$ also exhibit low dielectric losses up to 10^9 Hz. [49] Thus bismuth and strontium titanate films can be used as microwave condensers by virtue of their frequency characteristics and the comparatively low temperature at which they are prepared (<600°C), which is compatible with other technological operations.

It has been established [209] that thin layers of ferroelectric oxides with added lanthanum, having high and positive temperature coefficients of resistivity, can be used as sensitive detectors of infrared radiation. After annealing at 1400°C, a $Ba_{0.600}Sr_{0.397}La_{0.003}TiO_3$ film 10 μm thick had a resistivity of $\sim 10^6\ \Omega$ cm and a temperature coefficient of resistivity of ~6%. High annealing temperatures are an obstacle in the technology of the preparation of such elements for infrared video devices, but in the search for new thermistor compositions, technological progress should lead to the solution of this problem [210].

The pyroelectric materials usually employed as sensitive thermodetectors and in thermal vision systems consist of single crystals or ceramics, but the optimum thickness of such elements in thermal vision is 10–15 μm, i.e. the element should be a film. A decrease of thickness gives a higher sensitivity, a better resolution, and low inertia [211]. One of the problems arising in connection with the use of pyroelectric materials in such devices involves difficulties in the preparation of electrically and optically homogeneous elements of large size.

Piezoelectric elements made of massive ferroelectric materials are widely used as electromechanical transducers in acoustic arrest lines, but their comparatively large size limits their use to low frequencies. It has been shown [212] that elements ~1 μm thick are necessary in devices where the transducer operates as a generator or detector of ultrasonic waves at frequencies of $\sim 10^9$ Hz.

Thus ferroelectric films with high electromechanical coupling coefficients, such as $LiNbO_3$, lead zirconate-titanate, and alkali and alkaline earth metal niobates with the structure of tungsten bronzes can be used in such applications. Positive results have been obtained [183] on oriented $LiNbO_3$ films prepared by cathodic sputtering, in which the (012) plane of the hexagonal structure is inclined at an angle of 40° to the support. Piezoelectric measurements on thin films yielded a piezoelectric coefficient of 0.08, which amounts to about 50% of its value for the single crystal. The reasons for the difference are probably associated with the non-stoichiometry and inadequate structural ordering of the condensates.

By analogy with ferromagnetic materials, the ferroelectric hysteresis loop has a potential application in memory devices. It has been shown [177,213-216] that memories with capacities up to 10^9 bits can be achieved with the aid of thin photoconducting and ferroelectric layers. The thickness of the $(Pb_{0.92}Bi_{0.07}La_{0.01})(Fe_{0.405}Nb_{0.325}Zr_{0.27})O_3$ layers used, prepared by ceramic casting and sputtering [217], reached several micrometres, the ferroelectric films exhibiting a rectangular hysteresis loop and satisfactory thermal scattering. The memory device was charged by means of a light spot focussed on the screen of a cathode ray tube.

The use of thin ferroelectric layers in image-producing devices requires structures in which the contrast of the image, caused by the variation of double refraction under the influence of an electron beam modulated by the video signal, is not too sensitive to the thickness of the element. Here the most suitable material is bismuth titanate in which the optimum contrast can be achieved for a particular growth orientation. Since natural $Bi_4Ti_3O_{12}$ crystals do not grow in the required [crystal] habit, a solution was found to the problem when layers of the *A–C*-domain crystal with a large area (1 cm^2) were grown on MgO and $MgAl_2O_4$ single crystals [188,189,191]. An example of the use of a non-linear ferroelectric capacitance and of hysteresis properties in image-producing devices is provided by a

system comprising a liquid-crystal matrix and a thin transparent plate of a CTS ceramic with added lanthanum [218].

Among other applications, mention should be made of the use of ferroelectric films as indicator devices [219] and light modulators ($LiNbO_3$ and $LiTaO_3$) [220,221] and also for dielectric thermostabilisers and other purposes [222].

In conclusion one should note that, as a result of the efforts made in recent years to study the mechanisms of growth and ordering processes and to extend and improve preparative methods, there has been a clear progress in the technology of the preparation of highly ordered ferroelectric films, including epitaxial layers. However, many problems, on the solution of which depends the attainment of optimum properties (stoichiometry and homogeneity of composition, epitaxial growth, physical material of the electrodes, and methods of their deposition), are still far from a complete solution. There is a need for more far-reaching studies of the surface phenomena in ferroelectric materials, the role of which is particularly significant in a thin layer.

There has been an appreciable increase in the number of new ferroelectric films. Whereas the vast majority of studies were previously concerned with barium titanate, in recent years more than 20 new compounds and solid solutions have been obtained as films, including bismuth titanate, lead germanate, and antimony orthoniobate. Here efforts should be directed towards the search for compositions which do not require high temperatures of synthesis and which possess the necessary properties.

In practical applications there has been a transition from the predictive stage to the incorporation of thin-layer ferroelectric elements in solid state devices. The optimum technology has been developing vigorously recently. Further progress in research on thin ferroelectric layers will reveal new fields for their application.

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During the preparation of the manuscript for the press, numerous studies were published on the synthesis and applications of thin lithium niobate layers. $LiNbO_3$ films have been prepared by decomposing the vapours of organometallic compounds on lithium tantalate supports [226], by dipping the support in an $LiNbO_3$ melt [227], by diffusion into the region of the surface layer of the crystal [228-234], and by ion exchange [235]. Similar systems have been proposed as optical and acoustic waveguides and electro-optical modulators [230,231,236-246]. The applications of films as waveguides have been reviewed [247,248].

Memory devices based on films with an epitaxial structure (bismuth titanate), synthesised by high-frequency sputtering, have been made [249,250]. The possibility of devising capacitive film heat sensors has been demonstrated [251]. New data for size effects in ferroelectrics and their treatment in thin layers have been published [252,253] as well as data obtained in studies on $SrTiO_3$ and (Ba, Sr)TiO_3 vacuum condensates [254-256]. Methods have been developed for the measurements of the dielectric parameters of ferroelectric films in the ultrahigh frequency range [257].

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