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Formation of $LiNbO_3$ powders and thin films by hydrolysis of metal alkoxides

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Crystalline $LiNbO_3$ was prepared by simultaneous hydrolysis of lithium and niobium alkoxides (in the mole ratio Li : Nb = 1 : 1) followed by heat treatment. Crystallization of $LiNbO_3$ occurs in a wide temperature region, 350 to 700° C, directly from an amorphous hydrolysis product containing residual alkoxy and hydroxy groups. Heat treatment at 700° C results in the formation of fully crystalline $LiNbO_3$ powder with completely formed ferroelectric properties. Hydrolysis of metal alkoxide solutions is successfully used to obtain high-quality $LiNbO_3$ crystalline thin films.

1. Introduction

The hydrolysis of metal alkoxide solutions for the synthesis of complex oxides is attracting much attention these days. Application of this method leads to a substantial lowering of phase formation temperatures and an improvement of the physicochemical properties of the powders. It offers a convenient way of preparing highly homogeneous, chemically active fine powders. This method was successfully used earlier in the synthesis of ferroelectric materials such as $BaTiO_3$, $LiTaO_3$ and lead zirconate-titanate (PZT) or lanthanum modified lead zirconate-titanate (PLZT) solid solutions [1–3]. The application of metal alkoxide solutions proved to be especially useful for the formation of thin oxide films [4, 5]. Usually $Si(OR)_4$ and $Ti(OR)_4$ alcohol solutions were used to obtain thin amorphous oxide films. On the other hand more and more attention is being attracted now by complex oxide films with ferro-piezoelectric, magnetic and other physical properties, their characteristics being strongly dependent on the peculiarities of their structure. However, the problem of crystallization in the thin films obtained from solutions remained unsolved. It is well known that in the course of the crystallization of such films their smoothness and continuity is frequently destroyed.

In the present work a detailed study of the $LiNbO_3$ crystallization process was carried out, and the crystallization conditions and origin of the ferroelectric properties are discussed. Special attention was paid to the problem of crystalline $LiNbO_3$ film formation from alcohol solutions.

2. Experimental procedure

2.1. Powder synthesis and characterization

Taking into consideration the sensitivity of lithium and niobium alkoxides towards moisture and CO_2, all the procedures of preparation of their alcohol solutions were carried out in an atmosphere of dry argon.

Lithium niobate powders ($LiNbO_3$) were synthesized by the hydrolysis of solutions containing the double metal alkoxide $LiNb(OEt)_6$ ($Et = C_2H_5$) formed by the reaction of LiOEt and $Nb(OEt)_5$ in alcohol. This solution was hydrolysed by an aqueous ammonia solution added dropwise with stirring at 20° C. After the end of precipitation the stirring was continued for a further 15 min. The solution over the precipitate contained lithium (as a result of hydrolysis of the formed $LiNbO_3$), its quantity varying with the concentration of the precursor solution and amounting to 30% of the total lithium content of the system. Therefore the decantation procedure usually used for the isolation of other alkali niobates [6] cannot be applied here. We isolated the $LiNbO_3$ product by evaporation of solvent at 100° C followed by the drying of the residual powder at 150° C. The elemental analysis (wt %) for the powder obtained is 53.1% Nb, 2.7% C, 1.8% H and 84.5% $LiNbO_3$, and corresponds approximately to the composition $LiNbO_{2.9}(OC_2H_5)_{0.2} \cdot 1.1H_2O$.

Thermal analysis was carried out in air at a rate of $6° C\,min^{-1}$ and showed a weight loss in the temperature region 350 to 500° C. A broad exothermal peak on the DTA curve was observed in the same temperature range, corresponding to the elimination of the residual alkoxy groups from the precipitate. After heat treatment at 500° C for 20 min, a pure $LiNbO_3$ phase (Nb = 62.8%) containing less than 0.2% C is formed with the hexagonal lattice ($a = 0.3149(2)$ nm, $c = 1.386(2)$ nm), coinciding with the literature data [7].

Crystallite size distribution functions were obtained from X-ray line profile analysis [8]. The calculations were performed in the assumption that there were no defects or stresses. The $(1\,1\,\bar{2}\,6)$ line of $LiNbO_3$ was carefully recorded by the step-scanning technique with steps of 0.02° on the 2θ scale. The counting times provided for recording 10^4 counts at the peak. The angular range was five to six times the line width. Corrections for instrumental and spectral broadening

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TABLE I Conditions of crystalline $LiNbO_3$ film formation on quartz substrates

Fig. 5	Concentration of precursor solution (wt %)	Number of applications	Heat-treatment procedure (400° C, 15 min)	Storage time for the solution	H_2O (wt %)	Microstructure
(a)	10	1	Single	1 h	–	Cracks
(b)	5	4	After the application of each layer	3 weeks	–	"Bubbles"
(c)	5	4	As above	1 h	–	Smooth
(c)	5	4	As above	1 h after the dilution of a concentrated (35 wt %) solution stored for 3 weeks	–	Smooth
(d)	5	4	As above	1 week	1.5	Very deep "bubbles"

were made by means of data from $LiNbO_3$ single crystals.

Electron diffraction and electron transmission microscopy study of the powders was carried out (JEM-100CX); powders were dispersed for 10 to 15 min in alcohol prior to the investigation. Since highly dispersed particles tend to agglomeration, dark-field as well as the commonly used bright-field micrographs were employed for the evaluation of true crystallite size.

The second harmonic generation (SHG) technique was used in studying the ferroelectric properties of the fine powders. It is well known [9, 10] that this method proves to be especially useful for the evaluation of non-centrosymmetric phases. The measurements were carried out using a Q-switched Nd-YAG laser operating at 1.06 μm with the peak power about 1 MW. The powder sample under investigation was heated from 150 to 950° C at the rate of 20° C min^{-1}. Simultaneously laser-beam sounding was performed and reflected light with a doubled frequency was detected. The sensitivity of the detection was about 10^{-3} of the standard signal of quartz with a dispersity of 1 to 2 μm. The SHG technique is especially valuable in the present investigation as it gives an opportunity to register the signal continuously in the course of ferroelectric phase crystallization.

2.2. Thin film preparation

Solutions of metal alkoxides in ethyl alcohol were applied to the centre of substrates rotating at a rate of 4000 r.p.m. The thickness of a one-layer film corresponds to 20 to 30 nm (measured ellipsometrically). Films more than 20 to 30 nm thick can be obtained by a repeated application of the alkoxide solution. The quality of the films was controlled by scanning electron microscopy (Jeol-2). The details of the procedure are summarized in Table I.

3. Results and discussion

3.1. $LiNbO_3$ crystallization and formation of ferroelectric properties of the powder

The X-ray data for the powder obtained after drying the precipitate at 150° C ("as-prepared") indicate the amorphous character of the product. On the other hand the electron diffraction patterns testify to the existence of $LiNbO_3$ crystallites smaller than 5×10^{-3} μm in the samples. In the course of the heat treatment, when the temperature exceeds 350° C separate particles with dimensions much larger than average are formed. This fact is clearly seen on the electron micrographs. According to the analysis of X-ray diffraction peak intensities (Fig. 1a, triangle symbols) and electron micrographs, $LiNbO_3$ crystallization occurs gradually in a wide temperature range of 350 to 600° C; crystallites with an average size of 0.01 to 0.02 μm are formed in the amorphous matrix. It is noteworthy that the residual alkoxy and hydroxy groups – the constituents of the amorphous matrix – are being gradually eliminated in the same temperature range (Fig. 1b). Thus a close correlation between the two processes of phase crystallization and alkoxy- and hydroxy-group elimination is evident. It should also be emphasized that no growth of the crystallites is observed in this temperature range; only above 550° C can a few large crystallites be observed on the electron micrographs, the fact being confirmed by the crystallite size distributions obtained from the X-ray profile analysis (Fig. 2a, circle symbols).

The appearance and gradual formation of ferroelectric properties of the powder is characterized by the temperature dependence of the SHG intensity ($I_{2\omega}$) (Fig. 1a, solid curve). The following correlation is true for the $I_{2\omega}$:

$$I_{2\omega} \sim N d_{\text{eff}}^2 \langle l^2 \rangle \qquad (1)$$

where N is the number of ferroelectric particles ($LiNbO_3$ crystallites), $\langle l^2 \rangle$ the average squared crystallite size and d_{eff} a function of the basic ferroelectric characteristic of the substance, its spontaneous polarization P_s. Thus the detection of second-harmonic signal at 330° C apparently indicates the appearance of a substance with ferroelectric properties ($d_{\text{eff}}^2 \neq 0$) at this temperature. The subsequent growth of $I_{2\omega}$ in the temperature range 350 to 600° C can be described by Equation 1, taking into consideration the established temperature dependences of N and l while $d_{\text{eff}} \sim P_s$ remains constant for $LiNbO_3$ crystallites.

Three more stages of $LiNbO_3$ crystallization can be

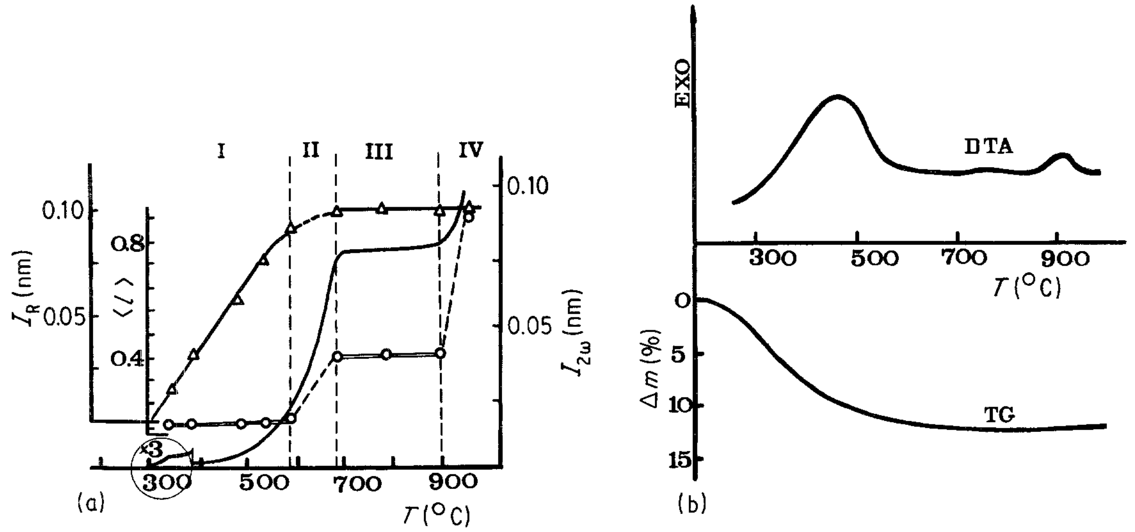

Figure 1 (a) The temperature dependences of (——) the SHG signal $I_{2\omega}$ of the $LiNbO_3$ powder obtained from metal alkoxide solution with regard to a ground single crystal with particle size 1 to 2 µm (the scale is magnified × 3 in the temperature region 300 to 400° C); (△) the intensity I_R of the X-ray diffraction peak with $2\theta = 23.7°$ $(1\,0\,\bar{1}\,2)$; (○) the average crystallite size $\langle l \rangle$ (µm) determined from electron micrographs. (b) Thermogravimetric data for the "as-prepared" $LiNb(OEt)_6$ hydrolysis product.

distinguished in Fig. 1. The second stage, restricted to the temperature range 600 to 700° C, is characteristic of an intense crystallite growth, the mean size of the particles increasing from 0.02 µm at 600° C to 0.3 µm at 700° C.

In the third stage (700 to 900° C), the powder is highly stable as far as crystallite size $(0.2 < 1 < 0.4\,\mu m)$ and ferroelectric properties are concerned. The value of the second-harmonic intensity is the same as for the samples obtained by fine grinding of $LiNbO_3$ single crystals. The fact indicates that their spontaneous polarization values are equal.

The fourth stage begins near 950° C and can be connected with the growth of certain crystallites by the absorbance of other smaller ones. In a narrow temperature region the crystallite size increases up to 1 µm and has a trend to further growth; a sharp exothermal peak on the DTA curve corresponds to this effect (Fig. 1b).

It is interesting to compare the electron microscopy results with the data obtained from the X-ray profile analysis (Figs 2 to 4). In the first crystallization stage, when the crystallites are small (0.01 to 0.02 µm) the data from the two methods are in perfect agreement (Fig. 2). Both methods demonstrate the increase of the average crystallite sizes in the powders heated at 550° C, though a certain number of small crystallites are preserved (Fig. 3). However, the X-ray profile analysis gives no evidence for the formation of larger crystallites in the case of powders heated at higher temperatures, though large crystallites are perfectly seen on the micrographs (Fig. 4). This apparent inconsistency can be resolved by taking into account the limitations of the X-ray method, which can be used successfully only for the size determination of small crystallites (~ 0.01 µm) [11]. Besides, the information obtained concerns not the real particle geometry but the average size of coherently diffracting domains, the latter being usually much smaller than the real size of the particles [11, 12]. The same is true for the SHG results: $\langle l^2 \rangle$ in Equation 1 stands not for the real size of the particles but for the domains in which the coherent non-linear interaction occurs. This is why the results of the two methods (X-ray profile analysis and estimation of crystallite size by SHG) are in perfect agreement, but these results should always be checked by electron microscopy. In the case of the $LiNbO_3$ crystallization they give correct information concerning the crystallite size distribution only in the first stage of crystallization when the crystallites are small (0.01 to 0.02 µm).

All the processes described are quick, as no essential differences in the powder characteristics were found when isothermal temperature conditions (from 10 or

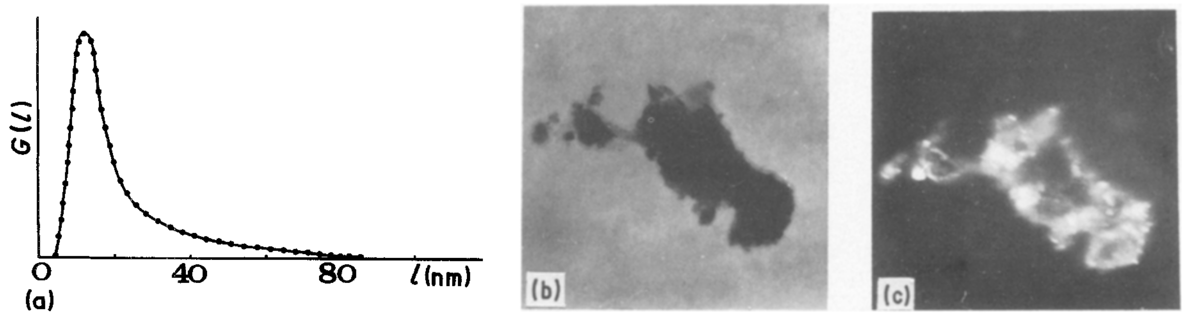

Figure 2 (a) Size distribution of the coherently diffracting domains obtained by the X-ray profile analysis, and transmission electron micrographs (× 100 000) in (b) bright and (c) dark fields; powder annealed at 400° C.

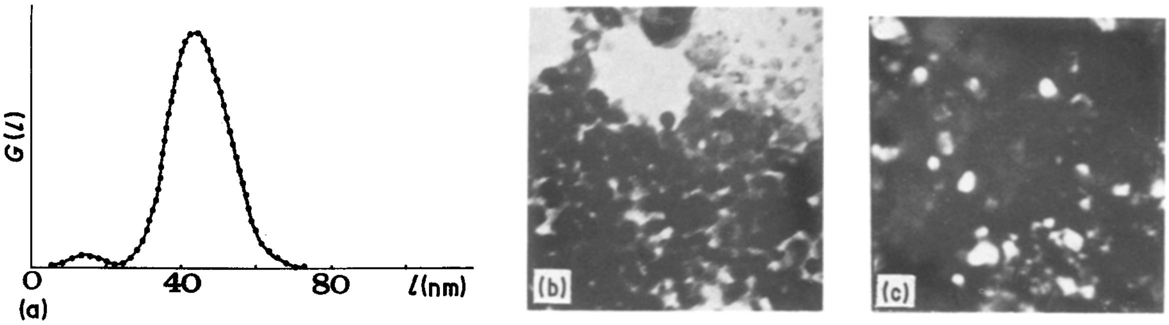

Figure 3 (a–c) As Fig. 2, annealed at 550° C.

15 min to 1 h) instead of dynamic treatment (heating at a rate of 20° C min^{-1}) were used. Prolonged thermal treatment leads only to an insignificant shift of the temperature boundaries between the crystallization regions.

The data obtained allows us to state quite definitely the chemical route of $LiNbO_3$ formation from metal alkoxides. Two different ways of complex oxide formation from the metal alkoxide hydrolysis products are known. $MgAl_2O_4$ spinel synthesis can be considered as an example of the first route: it is formed as a result of high-temperature chemical reactions between MgO and Al_2O_3 formed in the first stage of the thermal treatment of the hydrolysis product [13]. On the other hand, $BaTiO_3$ is formed by the hydrolysis of $BaTi(OEt)_6$ without any intermediate products [14].

The electron diffraction data for $LiNbO_3$ hydrolysis products testify to the low-temperature formation of $LiNbO_3$. No intermediate products were detected in the course of crystallization, thus excluding high-temperature solid-state reactions. The hydrolysis product is a complex lithium–niobium hydroxide containing a certain amount of alkoxy groups, its dehydration leading directly to $LiNbO_3$. The appearance of ferroelectric properties coincides with the formation of $LiNbO_3$ crystallites with a particle size of 0.01 μm or more. Apparently ferroelectricity as a cooperative effect of multi-ion interaction cannot be observed in the smaller particles.

3.2. The process of crystalline $LiNbO_3$ film formation

The process of film formation by the hydrolysis of metal alkoxide alcohol solutions consists of three main stages shown below: (I) application of the solution of the substrate, (II) dehydration of the thin film, (III) crystallization of the amorphous film:

$$\begin{array}{ccccc} & & \text{Mixture of} & & \\ \text{LiOEt} + \text{Nb(OEt)}_5 & \xrightarrow[-\text{ROH}]{\text{H}_2\text{O}+\text{CO}_2} & \text{hydroxides} & \xrightarrow[(-\text{H}_2\text{O},-\text{CO}_2)]{T_1} & \text{Amorphous} \\ & & \text{and} & & \text{film} \\ & \text{(I)} & \text{carbonates} & \text{(II)} & \text{(III)}\ \big\downarrow\ T_2 > T_1 \\ & & & & \text{Crystalline} \\ & & & & \text{film} \\ & & & & \text{LiNbO}_3 \end{array}$$

The influence of the following conditions on the quality of the films was studied:

(i) concentration of the solution;

(ii) successive operations of solution application and thermal treatment;

(iii) the presence of moisture traces in the solution and the "age" of the solution, that is the time passed from its preparation to the moment of utilization.

A significant change of the film density takes place in the crystallization process, thus leading to strict requirements as to the thickness of the film which can survive crystallization. All films obtained from solutions with concentration more than 10 wt % crack during crystallization (Fig. 5a). The same phenomenon is observed when a few amorphous layers, applied without thermal treatment after each layer, undergo

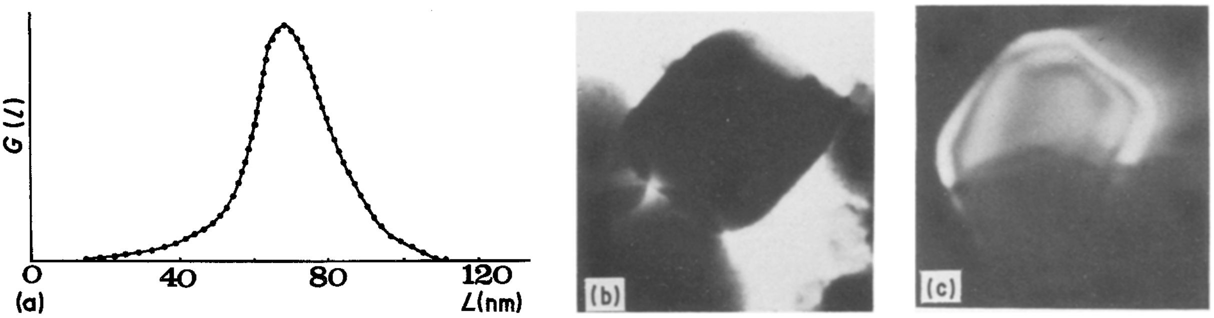

Figure 4 (a–c) As Fig. 2, annealed at 800° C.

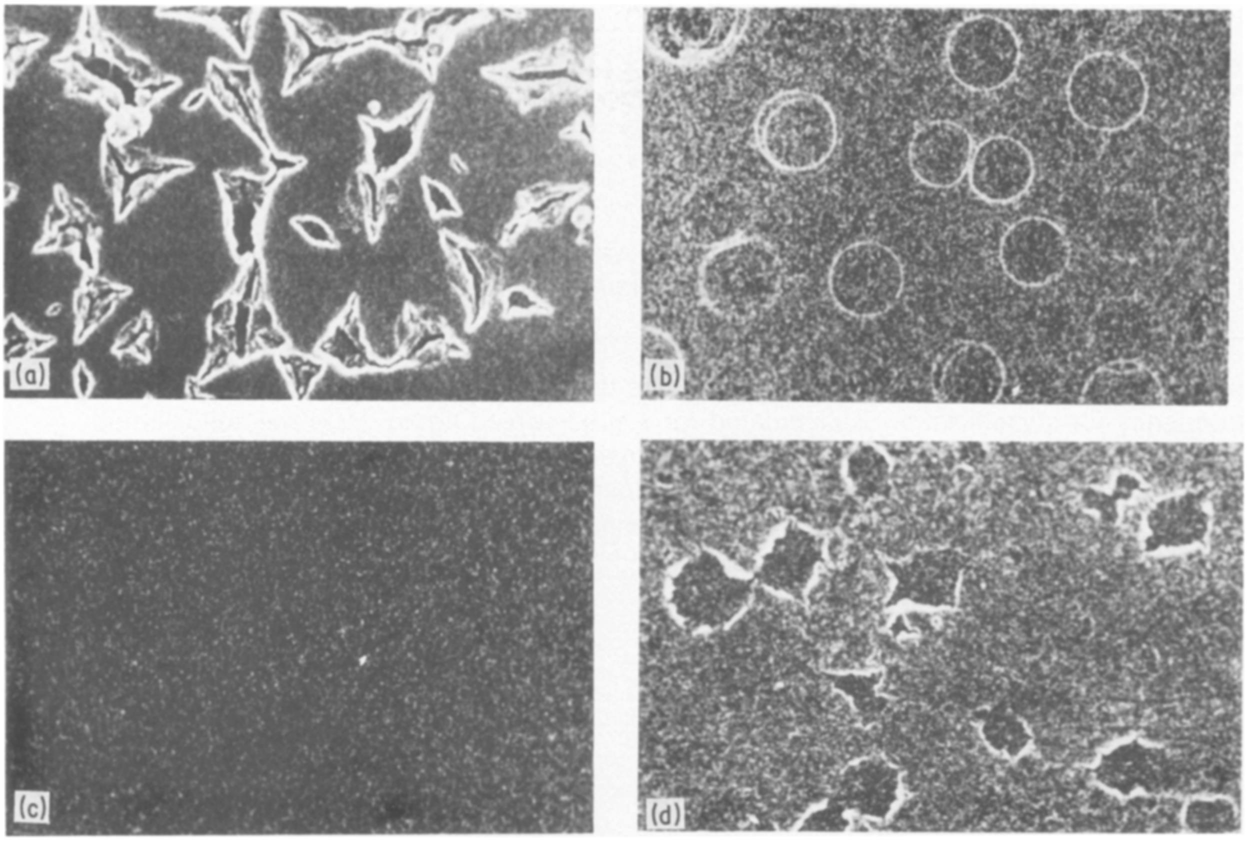

Figure 5 (a–d) Scanning electron micrographs (×8800) of crystalline $LiNbO_3$ films on quartz substrates; the formation conditions are summarized in Table I.

crystallization. High-quality crystalline films can only be obtained from diluted solutions (1 to 5 wt %) (Fig. 5c). Such solutions lead to the formation of films with a thickness 20 to 30 nm which survive crystallization without cracking. In order to obtain thicker layers, application should be repeated with obligatory heat treatment at 400° C for 15 min – the crystallization conditions for a thin film.

Utterly different types of defect in the crystalline films are caused by the existence of hydrolysis products in the precursor alcohol solutions. Insufficient drying of the solvent or prolonged storage of the diluted solutions before their utilization lead to the formation of "bubbles" (20 nm in depth) in the layer (Fig. 5b). The addition of a very small amount of water containing alcohol leads to a significant increase in the quantity of "bubbles", and application of the same solution a week after the addition of water spoils the surface completely (Fig. 5d). At the same time, application of a freshly prepared solution in ethyl alcohol previously dried with zeolite, ($Ca(OEt)_2$, $Ti(OEt)_4$) subsequently leads to the formation of films without any "bubbles"*. Concentrated solutions (30 to 40 wt % of $LiNb(OEt)_6$) may be also used which are stored in sealed or perfectly closed vessels; the solution should be diluted directly before usage. Even the films obtained by sticking to all of the above-mentioned conditions are not quite free from a certain quantity of fine "bubbles", the latter however being healed by subsequent layers of film. The best samples on platinum substrates with a thickness of 0.15 to 0.20 μm withstand an electrical voltage of $\sim$2 V.

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*It is noteworthy that a positive influence of H_2O was observed in the case of application of $Si(OR)_4$ and $Ti(OR)_4$ solutions (the ratio $[H_2O]:[Ti(OEt)_4]$ being from 0.5 to 7) for amorphous film formation. Moreover, in these cases a certain period of time from preparation till application of the solution (from a few hours to several days) is recommended.