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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF LEAD AND BARIUM TITANATE MATERIALS PREPARED BY THE SOL-GEL METHOD

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Abstract

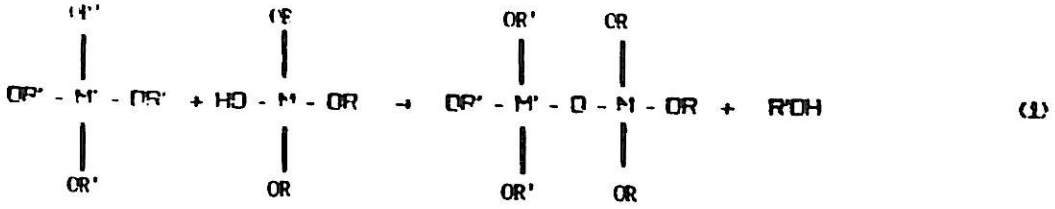
Sol-gel processing represent a promising method for the fabrication of dielectric materials. In this study we review the preparation and characterization of lead and barium titanate derived materials in form of gels, powders and films. The relative merits and problems of the different processing techniques are investigated. The physical properties of these materials obtained either in the amorphous or crystalline form and possible applications of technological interest are finally presented.

I Introduction

The fabrication of high quality ceramic materials and devices has received much attention in the recent years The chemical methods appear very attractive as they offer potential advantages over the traditional mixed oxide routes. In particular the purity, the chemical homogeneity and particle size characteristics may be all enhanced by adopting these processing techniques. These methods may also lower considerably the ceramic processing temperatures and therefore facilitate their integration with semiconductor devices, microelectronic packaging, integrated optics devices etc. This will include thin or thick layer devices and multilayer configuration. On the other hand the preparation of submicron powders with well defined and controlled granulation may lead to the obtention of better and more reliable ceramics with reproducible characteristics

In this paper we review the studies realized during the last decade using the sol-gel route for obtaining lead and barium-titanate derived materials in form of gels, powders, and films We first discuss the relative merits and problems of the different chemical processes used for the preparation of adequate precursors and for which two basic methods can be visualized:

a) a multicomponent alkoxide can be prepared by reacting a combination of single alkoxide The reaction of a partially hydrolised alkoxide of species M with another alkoxide of species M' forms a double alkoxide and an alcohol :



(1)

This method requires alkoxides of both species and an understanding of their relative rates of hydrolysis and reaction products.

b) a soluble salt such as a nitrate, acetate, etc can be added to a single or a complex alkoxide. An understanding of the solution and reaction chemistry of the species is important to determine the nature and the structure of these complex alkoxides and to obtain a stable sol.

We also discuss how to obtain specific sols from these precursors in order to prepare specific products such as gels, powders and films. Finally the physical properties of these materials obtained either in the amorphous or crystalline form are presented and possible applications of high technological relevance are commented

2 Lead Titanate derived materials

Pure lead titanate has not proved to be an important technological material when prepared via conventional processing procedures However it is the base constituent of important electrical ceramics such as PZT, PLZT, and its obtaining in thin film form of high optical quality and high refraction index may be fundamental for the development of electronic and optical devices.

2.1 Precursors and sols preparations

The first preparation of $PbTiO_3$ precursor was made by Gurkovich and Blum [1] through the reaction of lead acetate $Pb(C_2H_3O_2)_2$ dissolved in methoxyethanol $C_3H_8O_2$ with titanium isopropoxide $Ti(OC_3H_7)_4$ The synthesis process was rather complicated and the final product highly viscous with high moisture reactivity. Sols were prepared by dissolving this complex in

methoxyethanol (1:7 ratio volume) introducing the water of hydrolysis as a solution of methoxyethanol and water (2:1 ratio) with 0,002 mole HNO_3/mole water added. Gelation occurred in a few minutes and transparent gels were obtained after drying at 34°C for 2-3 weeks. Tetragonal $PbTiO_3$ was reported after firing at 600°C

The precursor preparation process was later modified by Budd et al [2,3] who recognized, through gas chromatography analysis, the occurrence of an exchange reaction between the titanium alkoxide and the methoxyethanol :

$$Ti(OR)_4 + 4(ROH) \rightarrow Ti(OR')_4 \rightarrow 4R'OH \qquad (2)$$

with R = iC_3H_7 and R = $CH_3OCH_2CH_2$

The titanium methoxyethoxide prepared in this way at 125°C was then combined with a 2-methoxyethanol solution of dehydrated lead acetate, reacted and concentrated by repeated vacuum distillations. Sols for gel formation and thin film preparation were prepared by combining equal volume of the stock solution with a solution of water-catalyst (acid or base) - methoxyethanol to give 0.5 molar gel. Stable sols were obtained for a $H_2O/PbTiO_3$ ratio smaller than 15. For higher ratio gelation occured in a few minutes with a rate increasing with the water amount and pH

We propose an easier method particularly useful to prepare precursor sol for the obtaining of dense material in film form. It is based on the chemical modification of titanium isopropoxide $Ti(OPr^i)_4$ by acetylacetone AcacH , a rather strong chelating ligand and stabilizing agent [4,5,6]. The preparation

of the complex alkoxide is described by the exothermic reaction [7]

$$Ti(OPr^i)_4 + 2\ AcacH \rightarrow Ti(OPr^i)_2(acac)_2 + 2\ Pr^iOH \qquad (3)$$

The yellow and homogeneous solution is mixed for 30 minutes until its temperature lowers to 25°C. A solution of lead acetate $Pb(OAc)_2\ 3H_2O$ in acetic acid (concentration 720g/l) is then added under 30 minutes stirring. This sol does not exhibit gelation or precipitation for at least 6 months. Its colour however changes from clear yellow to orange in a few days indicating either an evolution of the Ti complexation or a change in the particles size. Both precursor sols can be mixed in any proportion to prepare lead-titanate material of other compositions (Table 1).

Table 1

Typical composition for the preparation of $PbTiO_3$ and TiO_2 - 0.25 PbO sol

Product	Pr^iOH (ml)	acacH (ml)	$Ti(OPr^i)_4$ (ml)	Pb acetate solution (ml)	pH
$PbTiO_3$	40	3	4	7.24	4.7
TiO_2-0.25PbO	40	3	4	1.81	5.7

2.2. Gel to ceramic conversion

Whatever is the process of sol preparation, the dried gels are amorphous to X-ray up to ~ 400°C : their structure shows however differences analogous

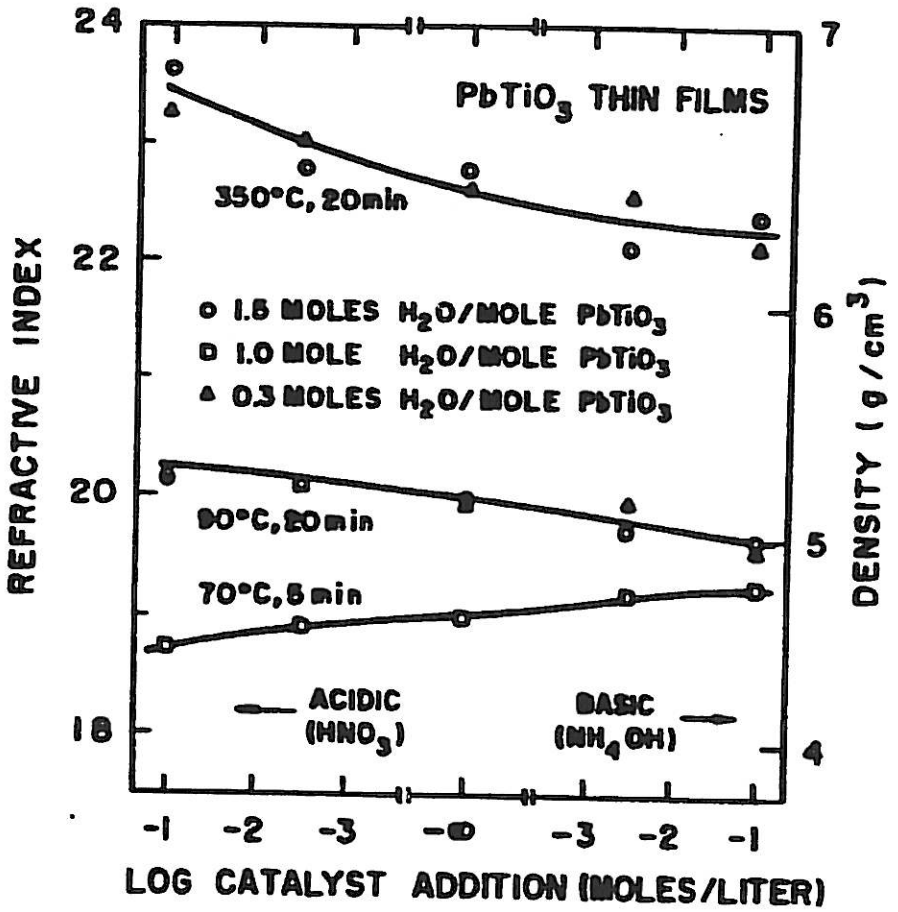


Figure 1 - Refractive index for amorphous $PbTiO_3$ thin films prepared by the sol-gel process as a function of the processing conditions from [3].

speed of 5 to 13 cm/min whatever is the ambient humity. Their index of refraction $n \simeq 2.05$ is however slightly smaller. Due to the easiness and the long life shelf of the sol preparation the $PbTiO_3$ and TiO_2 - PbO amorphous films are perfect candidates for the preparation of reflective coating (up to 45%) with flat characteristics in the visible or near infra-red region (Figure 2). The films deposited on glass have a lower index of refraction because of the diffusion of Na ions from the substrate during the heat treatment.

The fabrication of passive optical devices using the sol-gel method is simple and inexpensive. It has great advantages as the method allows to chose the index of refraction and the thickness of the layers. Hermann et al [10] have shown the feasibility of the method by fabricating planar optical waveguides using SiO_2 - TiO_2 Lipicoat Merck solution. Using a rutile prism coupler, a He-Ne laser beam was successfully coupled to a thin planar TiO_2 - 0,25 PbO film 0,82 μm thick deposited on a common glass substrate. Figure 3 shows the schematic arrangement and the dispersion relation of the thickness versus the effective mode numbers $N_m = n_p \sin\left(\epsilon + \arcsin(\sin\alpha/n_p)\right)$ [11] for the TE modes only. The values measured experimentally are in good agreement (Table II) :

Table II

Experimental values of α and N_m (see also fig 3)

TE_m	α	N_m
TE_0	18°38'	2.12
TE_1	11°12'	2.04
TE_2	-0°45'	1.89
TE_3	not observed	

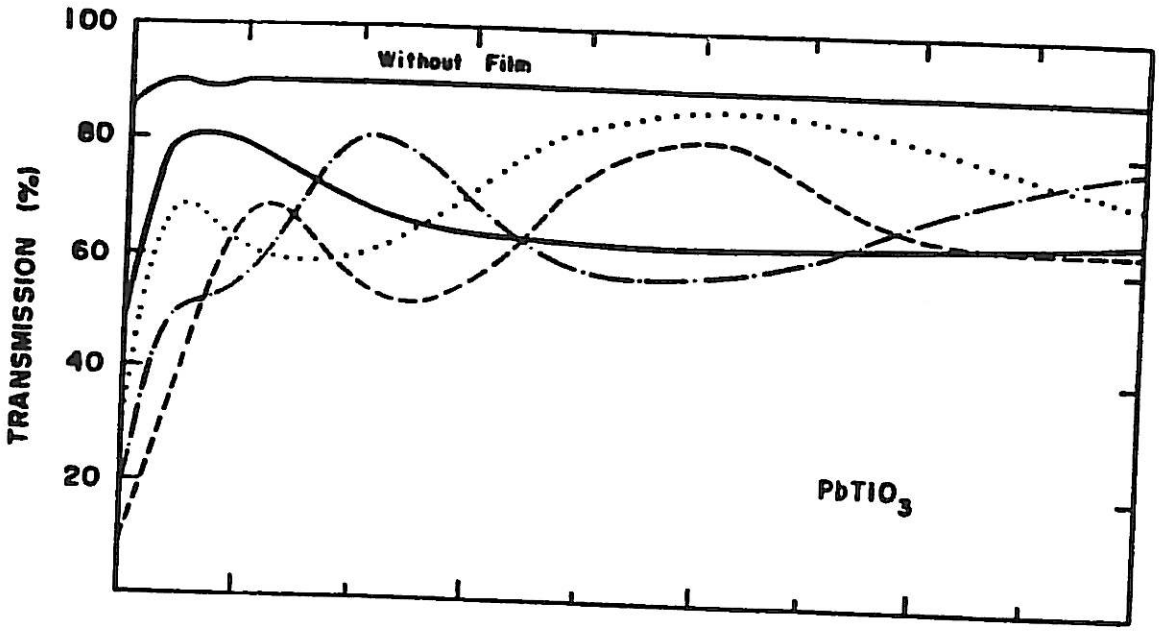


Figure 2(a) - Transmission spectra of films deposited on both facees of common glass substrate. Each layer is heat treated at 460°C during 15 min (top) $PbTiO_2$ ——— 1 layer, ····· 2 layers, -·-·-·- 3 layers, ----- 4 layers. Each layer has a thickness t - 72 nm.

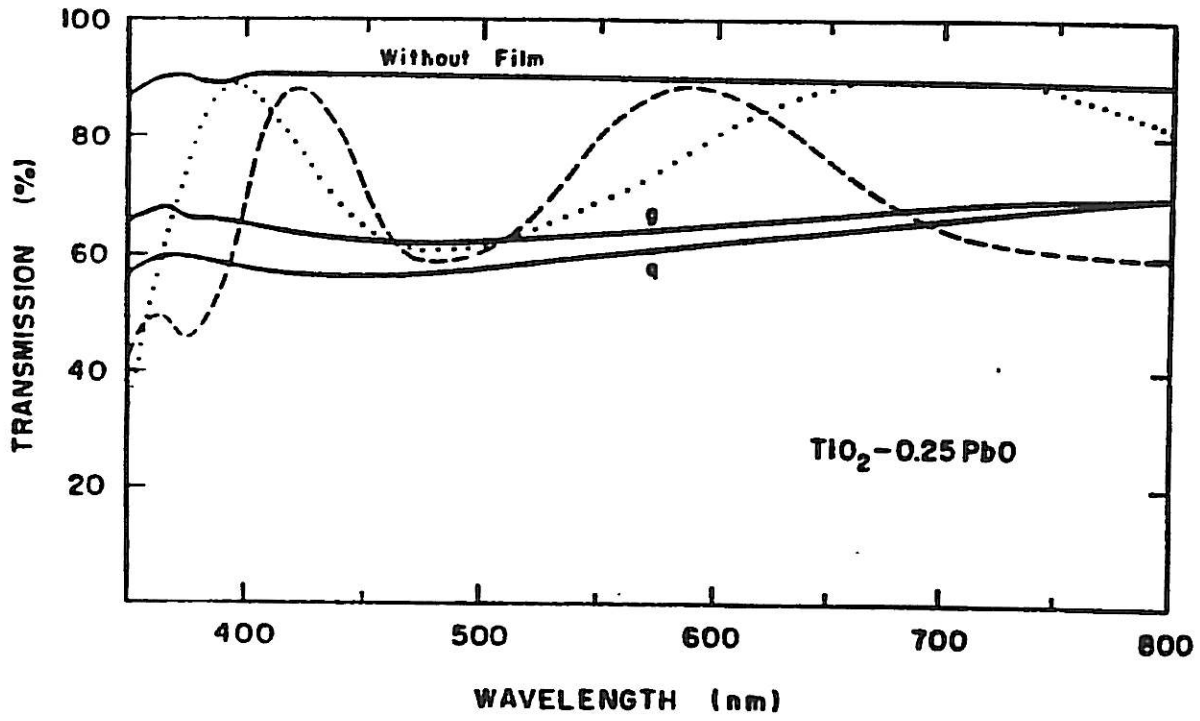


Figure 2(b) - TiO_2 - 0,25 PbO ___q___ 1 layer on a-quartz
t = 51 nm, n = 2.19, ___q___ 1 layer on glass
t = 55 nm, n = 2.10, ... 3 layers t = 170 nm,
n = 2.13, ----- 5 layers t = 280 nm, t = 2.17.

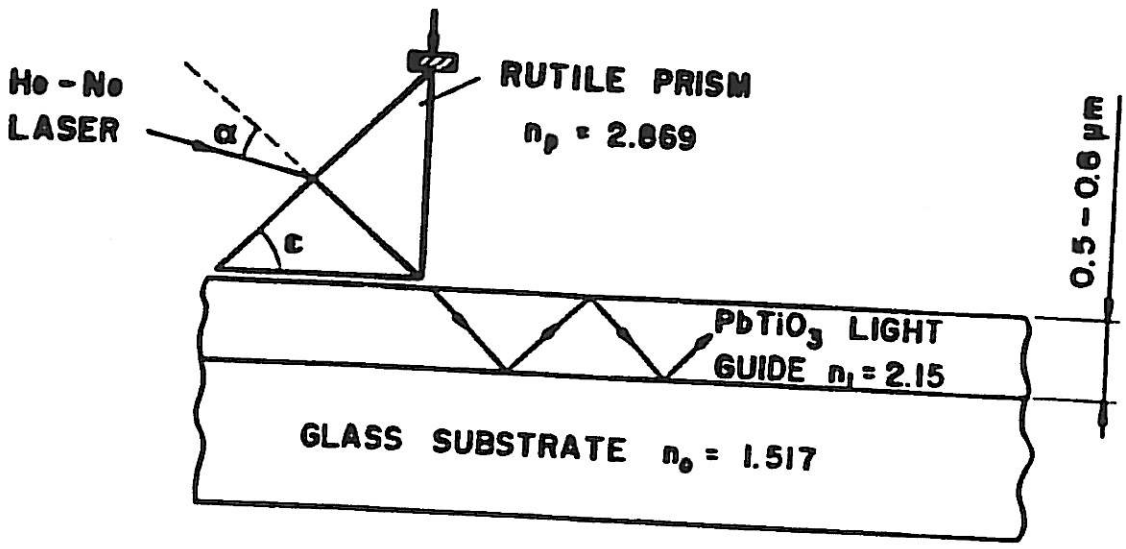


Figure 3(a) - Prism coupler method to couple He-Ne laser light beam to a TiO_2 - 0,25 PbO planar waveguide.

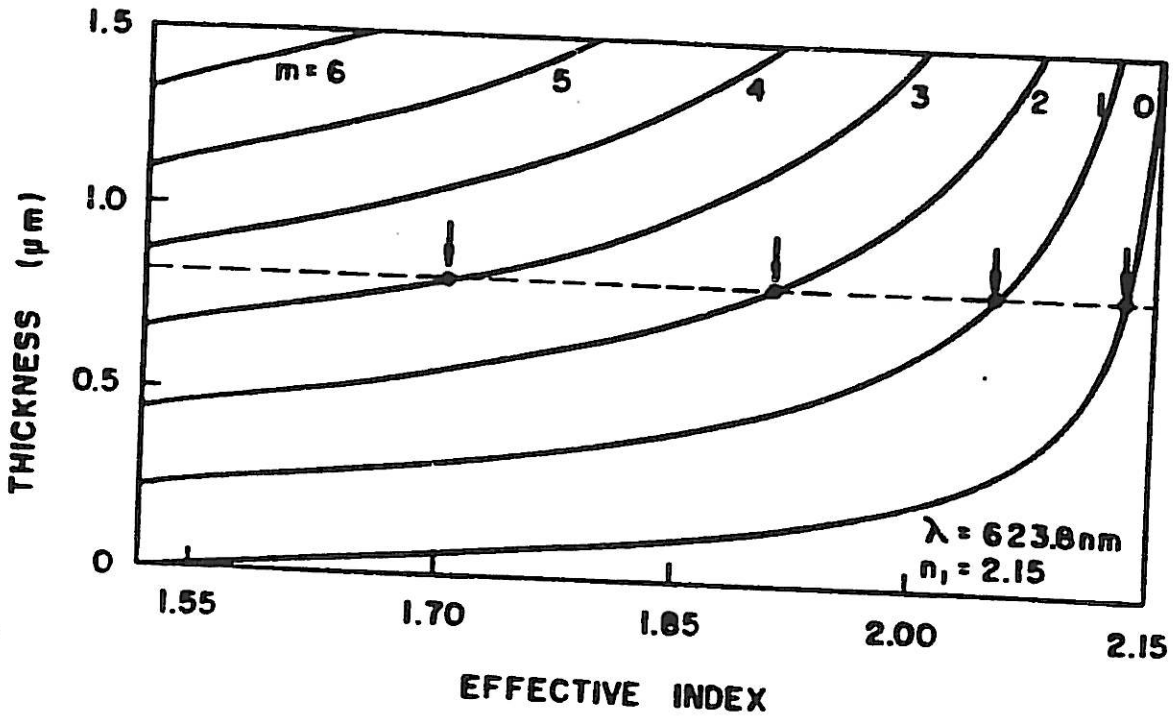


Figure 3(b) - Dispersion relation for a TiO_2 - 0,25 PbO waveguide (n_1 = 2.15 at λ = 623.8 nm) deposited on a glass substrate (n_o = 1.517) showing the various effective modes obtained as a function of the film thickness. The dashed line refers to a film 0.82 μm thick (15 layers) measured experimentally (see Table I).

These results are extremely promising and open a new field of application as the layers were prepared without special substrate cleaning, solution filtration and clean room facilities and confirm the high optical quality of these lead-titanate derived films.

Embossing techniques used in integrated optics to fabricate surface-relief gratings and channel waveguides would be another promising possibility. The technique was first developed for hard and resistant SiO_2 - TiO_2 sol-gel film (Liquicoat ZLI 1686 Merck) by Lukosz et al [12, 13] and more recently by Tohge et al for SiO_2 film [14]. The technique involves the pressing of a film against an aluminized reflective grating or stamper followed by baking at 500°C. The replica may function as input or output grating coupler, Bragg reflector, pregrooves of optical memory disk or any other optical device which requires an engraved pattern. Recently, using a micro processor controlled dipping arm to withdraw a SiO_2 - TiO_2 film from the solution with varying speeds, Hewak et al [15], fabricated tapered and lenslike waveguides. The successfull and easier preparation of thin lead titanate film of high optical quality combined with their high refraction index are without any doubt good candidates for future research and applications in this optical field.

3 Barium-Titanate derived material

Several compounds in the BaO - TiO_2 system are known to be technologically important electroceramics. $BaTiO_3$ is a dielectric ceramic widely used in the manufacture of capacitors. $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ have interesting properties for microwave applications (filters, etc). However the conventional processing of

these materials relies on relatively high temperature (1100 - 1300°C). It is therefore not surprising to find several sol-gel studies in the literature since the use of organometallic compounds allows in principle a low temperature preparation and processing of homogeneous thin films and powders without the undesirable impurities such Al_2O_3, SiO_2 S, P etc which have deleterious effects on the electrical properties of these ceramics

3.1 Review of sols and gel to ceramic conversion

3.1.1 Preparation using two alkoxides

In their pioneering work, Mazdiyasni et al [16,17] prepared $BaTiO_3$ powder by the simultaneous hydrolytic decomposition of high purity titanium tertiary butoxide $Ti(OC_5H_{11})_4$ and barium bis isopropoxide $Ba(OC_3H_7)_2$. The stoichiometric mixture of both alkoxides was refluxed for 24 h. After adding dropwise water and isopropyl alcohol they obtained a barium titanate oxalate precipitate which after washing and drying at 50°C gave a > 99.98% pure $BaTiO_3$ powder of 50 - 150 Å size. Doping with Sr an Ln oxide were prepared by addition of the respective isopropoxides. The powders were calcined at 500°C for 30 minutes, ground and then cold pressed. Sintering of compact bodies were done in air at 1300 - 1500° for 1h.

Thin films have been prepared by Yanovskaya et al [19] by hydrolytic decomposition of alcoholic solution of $Ba(OEt)_2$ and $Ti(OEt)_4$. These solutions are highly sensitive to moisture and carbon oxide. the formation of the perovskite structure is thought to arise from the hydrolysis of $BaTi(OEt)_6$ and crystallization into $BaTiO_3$ occurred around 700°C and several

polytitanates such as Ba_2TiO_4, $BaTi_2O_5$ and $BaTi_4O_7$ were observed at higher annealing temperature.

Rehspringer [19] prepared $BaTiO_3$ powders by mixing the same ethoxides in presence of a large excess of alcoholic water (400%) The reaction led to the formation of very fine amorphous powder (~ 30nm) already aggregated Crystallization occurred at ~700°C. Monolithic gels [19,20] were obtained by controlling the chemical reactions of hydrolysis and polycondensation by working at lower temperature (~ -45 - 0°C). After drying the gels can be transformed at 725°C into a glassy matrix containing small egg-shaped $BaTiO_3$ crystals

3.1.2 Preparation using BaO and Ti alkoxide

Ritter et al [21] proposed a novel and inexpensive technique that uses technical grade BaO to prepare a barium extract under argon atmosphere, this compound is thought to be a 1:1 mixture of $Ba(OC_2H_5)_2$ and $(C_2H_5O)Ba_2O$ and has been used in the preparation of barium polytitanates by reaction with titanium isopropoxide, ethanol and water. The powder which resulted was separated by centrifugation, washed and finally dried The method was used to prepare and characterize various polytitanates such as Ba_2TiO_4 (2:1) $BaTiO_3$ (1:1), $Ba_6Ti_{17}O_{40}$ (6:17), $Ba_4Ti_{13}O_{30}$ (4 : 13), $BaTi_4O_9$ (1:4) $Ba_2Ti_9O_{20}$ (2:9), $BaTi_5O_{11}$ (1:5) and $BaTi_5O_{13}$ (1:6)

3.1.3 Preparation using $Ba(OH)_2$

Flaschen [22] proposed an aqueous synthesis of $BaTiO_3$ by the dropwise addition of tetrapropyl titanate to a degassed water solution of barium

hydroxide (pH 11 to 14) This technique was found useful for introducing desirable impurities and for the partial substitution of barium. The process is simple and is summarized as follows :

$$Ba(OH)_2 + Ti(OC_3H_7)_4 \; H_2O \rightarrow BaTiO_3 + 4C_3H_7OH \qquad (5)$$

The same process was later used by Dosch [23] to prepare thin film on Si, Ni and Ti substrates

3.1.4 Preparation using Barium carbonate and Ti alkoxide

Salze et al [24] prepared powders with the following reaction : titanium was introduced in the form of Ti isopropoxide dissolved in ethylene glycol and citric acid. at 80 - 100°C. The clear and water soluble complex is not yet known. Barium was introduced as a solution of carbonate dissolved in citric acid at 80°C. The final solution is clear, water soluble and stable; a polymer can be obtained by heating at 160°C which after elimination of the organic fractions is pyrolysed in air. Crystalline $BaTiO_3$ is noted around 550°C together with $BaCO_3$ and other polytitanates. The powder is constituted of small plates 10µm thick composed of clusters of $BaTiO_3$ (~ 0,5 µm) associated with very small crystallites (20 - 40 nm).

3.1.5 Preparation using Ba acetate and Ti alkoxide

This recent method is quite interesting since it allows the preparation of powders and thin films from simple chemical polymerization between

inexpensive and moisture insensitive materials.

The process involves the mixing at room temperature of a solution of Ti isopropoxide in isopropanol [25,26,27] or Ti-ethoxide [28,29] with an aqueous solution of Ba acetate (molar ratio 1:1). Acetic acid and /or acetylacetone are also added in order to avoid precipitation These sols are relatively stable and gel in a few days. The white opaque gels transform into powder when dried at 100°C. Thin films can be prepared by the dip coating technique at a withdrawal speed 6 - 20 cm/min for a sol viscosity 2.5 - 4 cp For both products crystallization starts around 550° - 600°C The evolution of the local structure of the Ba- Ti environment of the complex has been studied by Mosset et al [28] by large angle X-ray scattering method They showed that for T ≤ 250°C $Ba_3(HC_3COO)_8$ units are associated to Ti_2 and Ti_4 complex molecules. Pyrolysis of the organic ligands with Ba-O-Ti bonds breaking occurs between 250°C and 400°C. The presence of $BaCO_3$ around 400°C and a theoretical analysis of the radial distribution function which excludes BaO, $BaTi_4O_9$ and Ba_2TiO_4 as precursors indicate that $BaTiO_3$ is probably formed by $BaCO_3$ - TiO_2 reaction. Gels dried hypercritically at 280°C, 200 bar and analysed by TEM and X-ray diffraction showed a needle structure composed of crystalline barium acetate and titanium oxide In this case pure $BaTiO_3$ was only observed after heat treatment at 900°C [25]

2.1.6 Other preparation

Alkoxide [30,31] have recently developed a promising new route to synthesize titanate compound powders from catecholate complexes through the following reactions:

$$\text{a) } TiCl_4 + 3\,C_6H_4(OH)_2 \xrightarrow{\text{dry toluene}} H_2[Ti(C_6H_4O_2)_3] + 4HCl \qquad (6)$$

$$\text{b) } H_2[Ti(C_6H_4O_2)_3] + BaCO_3 \xrightarrow[(100°C)]{H_2O} Ba[Ti(C_6H_4O_2)_3] + H_2O + CO_2$$

After removing the unreacted carbonate phases by filtration this sol was freeze-dried to isolate the complex in solid form and transformed by calcination at 600°C (1h) into a crystalline $BaTiO_3$ fine powder.

2.2 Gels, powders and films characterization

Most of the available characterization of the Ba-titanate derived materials are obtained by X-ray diffraction and TEM studies. Differences in alkoxide precursor, hydrolysis and polycondensation conditions, drying and calcination conditions, all have an important effect on the polymeric structure and subsequent ceramic microstructure. It is therefore difficult to synthesize the results.

Whatever is the precursor preparation the "$BaTiO_3$" initial product is amorphous but the structure of the chemical complex is not well known; when calcined at 500 - 600°C it transforms into crystalline $BaTiO_3$ with tetragonal structure. Adapting the stoichiometry it is possible to obtain other Ba-Ti compositions. At this stage the powders are usually composed of fine particles

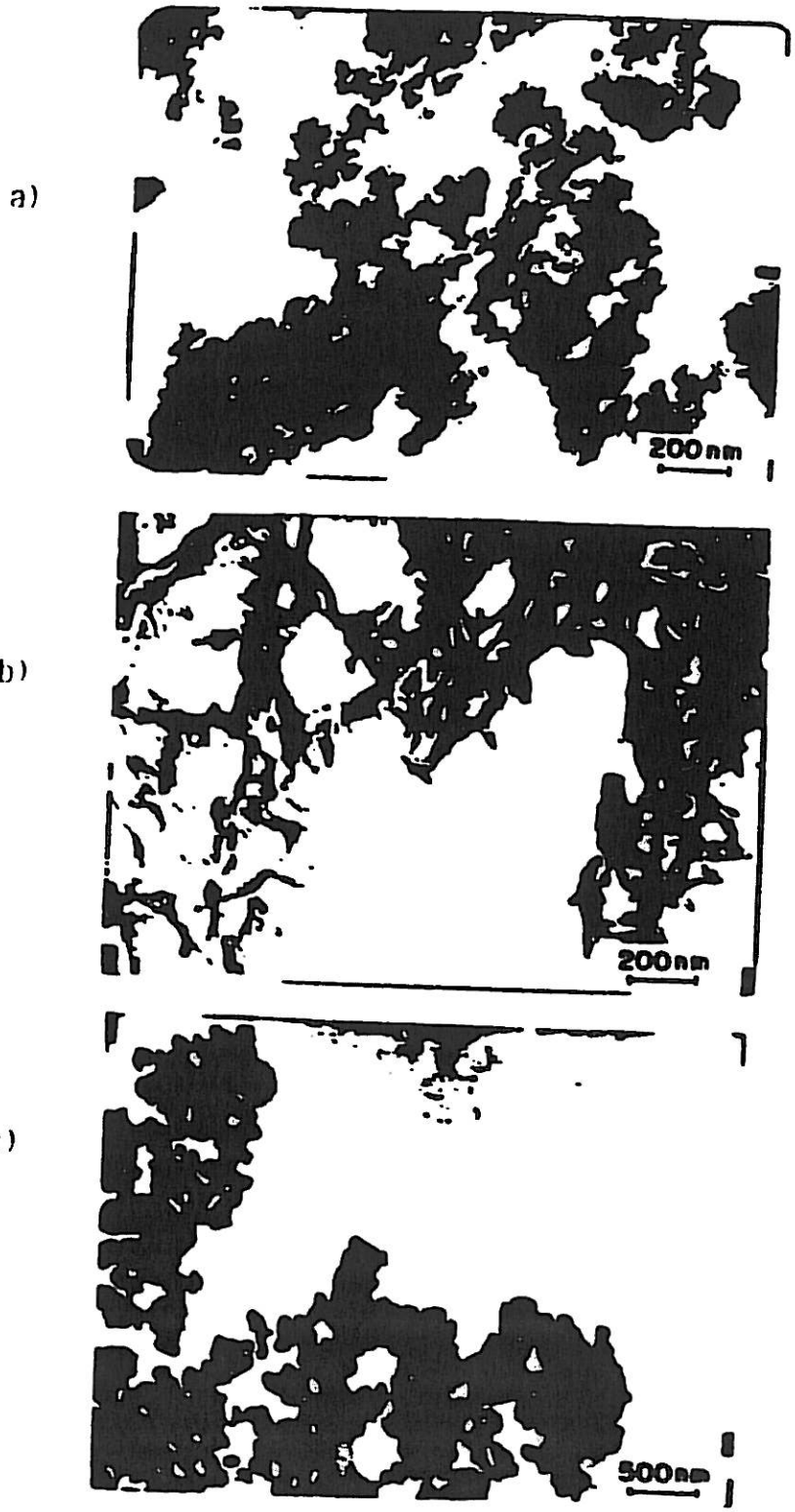
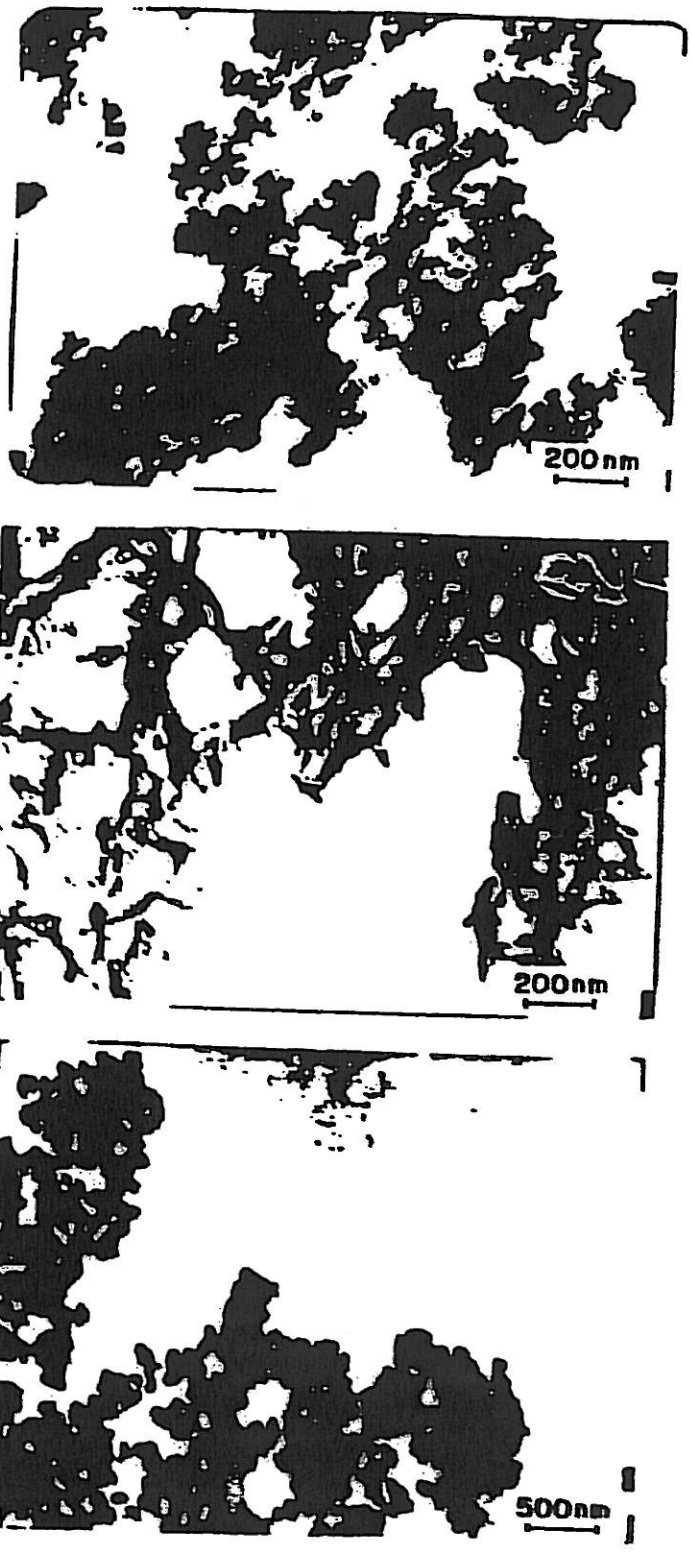


Figure 1 - $BaTiO_3$ powders structure obtained by the Ba acetate Ti isopropoxide method (see 3.1.5) and calcined at 700°C for 2h:

a) sol prepared at a pH = 4.3 and dried at 100°C
b) sol prepared at a pH = 9.4 and dried at 100°C
c) sol prepared at a pH = 4.3 and hypercritically



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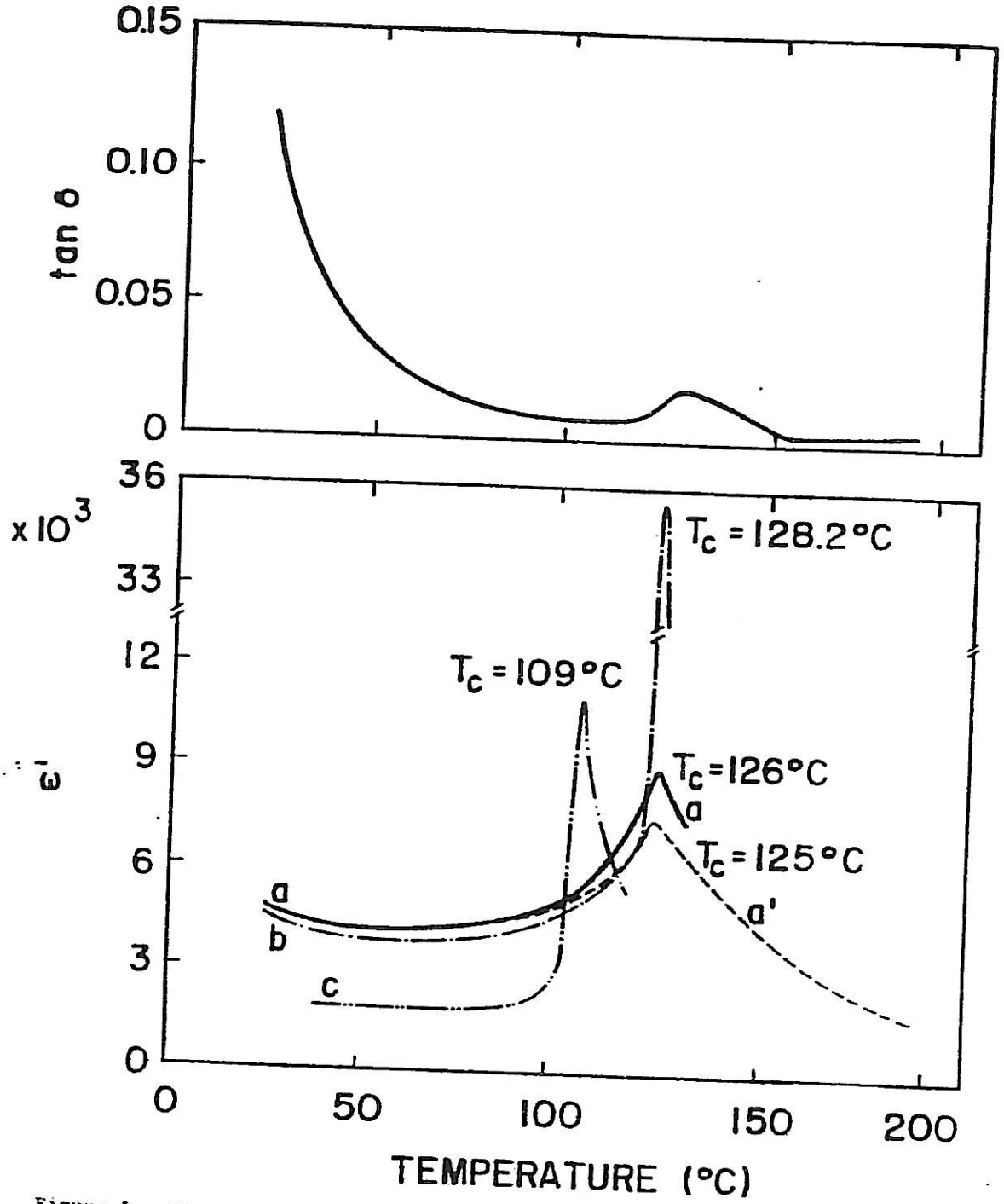

Figure 5 - Dielectric constant and dissipation factor measured as a function of temperature of pure $BaTiO_3$ ceramic prepared with:
a) and a') powder obtained from Ba Cetate and Ti isopropoxide mixture (see 3.1.5) calcined at 700°C and sintered at 1350°C, 2h (a') and 5h (a) (f = 10 KHz)
b) powder obtained from Ba and Ti alkoxide mixture (see 3.1.1) calcined at 50°C and sintered at 1350°C, 1h (from [17]).
c) powder obtained by the Solvay group [32] and sintered at 1325°C, 4h (precursor preparation and processing not available)

small discontinuity at the Curie point. Phule et al [20] have also reported that the powder calcined at 700°C and sintered at 1350°C for 6h have a dielectric constant of 4000.

Until now and in spite of their fundamental technological importance for the preparation of multilayer capacitors, $BaTiO_3$ obtained in thin films form has been poorly characterized. Dense amorphous single layer 30 to 120nm thick with index of refraction n = 2.0 can be deposited by dip coating technique on glass, a-SiO_2 and metallic substrates. Thick layers can be prepared by repeating the process. According to X-ray diffraction and DTA-TG results, crystallization into tetragonal $BaTiO_3$ structure occurs in the temperature range 450 - 500°C [23, 25] or 700°C [18]. Annealing at higher temperature only increases the grain sizes and no other titanate have been reported. Amorphous films have an electrical breakdown strength of the order of 9.10^5 V/cm, greater than of crystalline films ~ 10^5 V/cm, the values however are dependent of the substrate material [23, 18]. Manifestation of ferroelectric properties have only been reported after a heat treatment at 600°C where sufficient grains size of 0.1μm has been obtained. Higher temperatures increase the grains size but is accompanied by films cracking and formation of cavities. The dielectric response is poor (ε' ~ 50 - 60), tan δ ~ 2-3) and shows a broad Curie point at 118°C with little increase of the dielectric constant [19].

4 Conclusion

Sol-gel processing of lead and barium titanate materials is possible and various precursors preparations recipes are now available and have been

reviewed These materials can be better obtained in form of gels, powders and films Amorphous products are obtained at low temperatures but their chemical compositions and their thermal evolution are usually not known with certainty Basic and arduous work is still necessary in order to elucidate these processes.

All the materials crystallized at relatively low temperature (500 - 700°C). The transition temperatures depend mainly of the precursor preparation and the processing conditions.

However interesting dielectric properties seem only obtainable at temperatures close to those used in conventional processes but no detailed and systematic studies have yet been reported to optimize the processing conditions

The sol-gel process definitively lower the temperature of formation of pure lead and barium titanate derived materials but it not proven at all that devices having physical characteristics similar or better to those obtained today by conventional processes can be prepared by this method.

The most interesting results are reported for amorphous thin films densified at low temperatures . $BaTiO_3$ films present good electric insulation properties and lead-titanate films are promising systems for optical applications and passive integrated-optical devices fabrication.

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