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

M. A. AEGERTER, Y. CHARBOUILLOT, N. MOHALLEM, AND L. H. DE GODOY

53.1. 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 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, and so on. 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.

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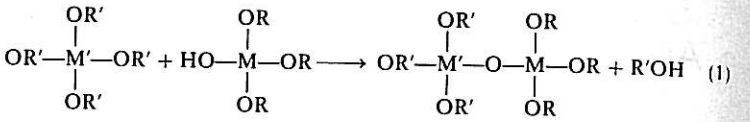
In this Chapter we review the studies realized during the last decade using the sol–gel route for obtaining lead and barium titanate-derived materials in the form of gels, powders, and films. We first discuss the relative merits and problems of the different chemical processes used for the preparation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

1. A multicomponent alkoxide can be prepared by reacting a combination of single alkoxide. The reaction of a partially hydrolized 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.

2. A soluble salt, such as a nitrate or acetate, 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 mentioned.

53.2. 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 lead zirconium titanate and PLZT. Its synthesis in a thin-film form of high optical quality and high refraction index may be fundamental for the development of electronic and optical devices.

53.2.1. 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, $C_3H_6O_2$ 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 mol HNO_3/mol water added. Gelation occurred in a few minutes, and transparent gels were obtained after drying at 34°C for 2 to 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:

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

where R′ = i-C_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 M gel. Stable sols were obtained for a $[H_2O]/[PbTiO_3]$ ratio smaller than 1.5. For higher ratios, gelation occurred 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 obtaining dense material in film form. It is based on the chemical modification of titanium isopropoxide $Ti(O\text{-}i\text{-}Pr)_4$ by acetylacetone (AcacH), a rather strong chelating ligand and stabilizing agent [4–6]. The preparation of the complex alkoxide is described by the exothermic reaction [7]

$$Ti(O\text{-}i\text{-}Pr)_4 + 2AcacH \rightarrow Ti(O\text{-}i\text{-}Pr)_2\,(Acac)_2 + 2(i\text{PrOH}) \qquad (3)$$

The yellow and homogeneous solution is mixed for 30 min until its temperature lowers to 25°C. A solution of lead acetate, $Pb(OAc)_2.3H_2O$ in acetic acid (concentration 720 g/liter) is then added under 30 min of stirring. This sol does not exhibit gelation or precipitation for at least 6 months. Its color, 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 53.1).

TABLE 53.1. Typical Composition for the Preparation of $PbTiO_3$ and TiO_2-0.25PbO Sol

Product	i-PrOH (ml)	Acetylacetone (ml)	$Ti(O\text{-}i\text{-}Pr)_4$ (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

53.2.2. Gel to Ceramic Conversion

Whatever is the process of sol preparation, the dried gels are amorphous to X-rays up to ~400°C. Their structure shows, however, differences analogous to those found for SiO_2 gels: Acidic gels have fibrous morphology with entanglements of more linear and less crosslinked species capable after drying of polymeric rearrangement into microcrystalline regions. The spatial repartition of Pb and Ti was found homogeneous. On the contrary, basic gels have a coarse texture and a more highly condensed structure and inhomogeneous cations distribution [3, 8]. These materials crystallize directly into a $PbTiO_3$ perovskite structure with crystallite sizes of 225 to 450 Å; the transition temperature is lower than that found in conventional processes and depends on the time of the heat treatment (typically 425°C after 600 min) [9]. The heat of crystallization for the basic gel is higher than for acid gel, and the reaction rate is given by the Arrhenius law $K = \exp(-E_a/kT)$, with $E_a \sim 63$ kcal/mol and $\nu = 1.72 \times 10^5\ \text{sec}^{-1}$ [9]. No structural and thermal characterizations are yet reported for films.

53.2.3. Properties and Applications

Some dielectric properties have been reported by Budd et al. [3] who found that partially ordered acid gels have a higher dielectric constant ($\varepsilon' \sim 36$–40) than base-catalyzed gels ($\varepsilon' \sim 28$–32) and that ε' is smaller for the crystalline material. The most interesting characteristics are related to the optical properties of thin films. Figure 53.1 shows the evolution of the refractive index as a function of the processing conditions [3]. Acidic film heated to 300°C have a higher value than corresponding base-catalyzed film, consistent with the concept of polymeric rearrangement leading to a denser structure.

The amorphous films obtained by us by a dip-coating technique and densified in air at 460°C for 15 min have outstanding optical quality when withdrawn at a speed of 5 to 13 cm/min whatever is the ambient humidity. Their index of refraction, $n \simeq 2.05$, is, however, slightly smaller. Due to the easiness and the long shelf life 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 infrared region (Fig. 53.2). 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 is advantageous as the method allows the choice of index of refraction and the thickness of the layers. Hermann and Wildmann [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_2–0.25PbO film 0.82 μm thick deposited on a common glass substrate. Figure 53.3 shows the schematic arrangement and the dispersion relation of the thickness versus the

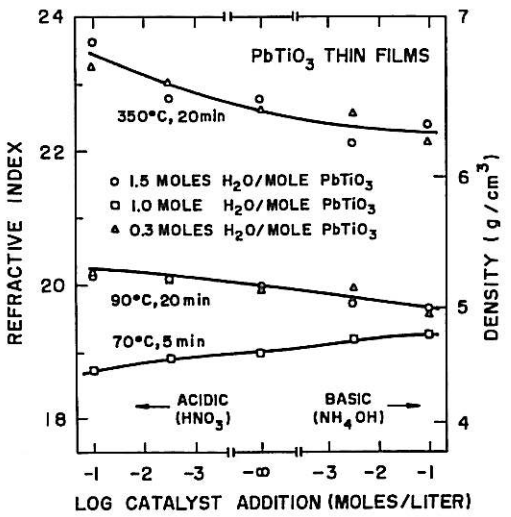


Figure 53.1. The refractive index for amorphous $PbTiO_3$ thin films prepared by the sol–gel process as a function of the processing conditions from Ref. 3.

effective mode numbers $N_m = n_p \sin(\varepsilon + \arcsin(\sin\alpha/n_p))$ [11] for the TE modes only. The values measured experimentally are in good agreement (Table 53.2).

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

TABLE 53.2. Experimental Values of α and N_m[a]

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	

[a]See also Fig. 53.3.

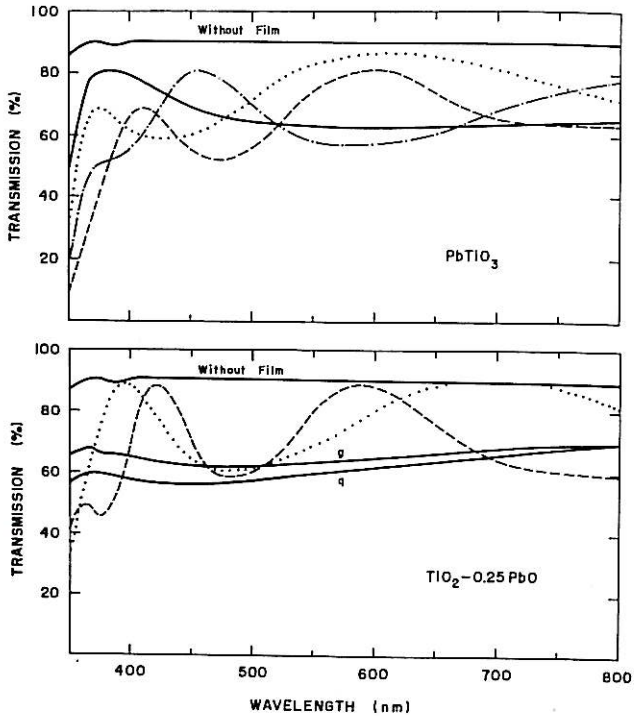


Figure 53.2. Transmission spectra of films deposited on both faces of common glass substrate. Each layer is heat treated at 460°C for 15 min. (Top) $PbTiO_3$: ———, one layer; ··· two layers, –·–·, three layers; – – –, four layers. Each layer has a thickness $t \sim 72$ nm. (Bottom) TiO_2–0.25PbO: q, one layer on α-quartz, $t = 51$ nm, $n = 2.19$; g, one layer on glass, $t = 55$ nm, $n = 2.10$; ···, three layers, $t = 170$ nm, $n = 2.13$; – – –, five layers, $t = 280$ nm, $n = 2.17$.

(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 dry film against an aluminized reflective grating or stamper followed by baking at 500°C. The replica may function as an input or output grating coupler, Bragg reflector, pregrooves of optical memory disk, or any other optical device that requires an engraved pattern. Recently, using a microprocessor-controlled dipping arm to withdraw a SiO_2–TiO_2 film from the solution with varying speeds, Hewak and Lit [15] fabricated tapered and lenslike waveguides. The successful and easier preparation of thin lead titanate film of high optical quality combined with their high refraction index is without any doubt a good candidate for future research and applications in this optical field.

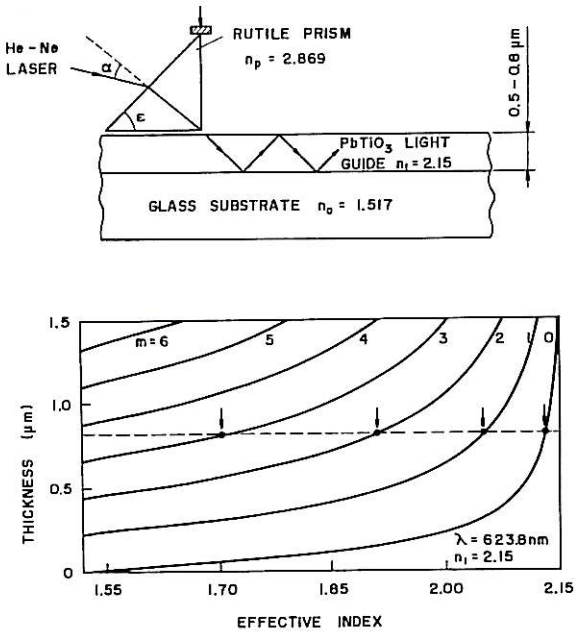


Figure 53.3. (*Top*) The prism coupler method to couple the He–Ne laser light beam to a TiO_2–0.25PbO planar waveguide. (Bottom) The dispersion relation for a TiO_2–0.25PbO waveguide ($n_1 = 2.15$ at $\lambda = 623.8$ nm) deposited on a glass substrate ($n_0 = 1.517$) showing the various effective modes 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 53.2).

53.3. 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, because 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, and P, which have deleterious effects on the electrical properties of these ceramics.

53.3.1. Precursors, Sols, and Gel-to-Ceramic Conversion

53.3.1.1. 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 amyloxide $Ti(OC_5H_{11})_4$ and barium bisisopropoxide, $Ba(OC_3H_7)_3$. The stoichiometric mixture of both alkoxides was refluxed for 24 hr. After adding dropwise water and isopropyl alcohol, they obtained a barium titanate hydroxide precipitate, which after washing and drying at 50°C gave a >99.98% pure $BaTiO_3$ power of 50- to 150-Å size. Doping with Sc, and Ln oxide was prepared by the addition of the respective isopropoxides. The powders were calcined at 500°C for 30 min, ground, and then cold pressed. Sintering of compact bodies was done in air at 1300 to 1500°C for 1 hr.

Thin films have been prepared by Yanovskaya et al. [18] by hydrolytic decomposition of alcoholic solution of $Ba(OEt)_2$ and $Ti(OEt)_4$. These solutions are highly sensitive to moisture and carbon dioxide; the formation of the amorphous product is thought to arise from the hydrolysis of the $BaTi(OEt)_6$ complex. Crystallization into $BaTiO_3$ occurred around 700°C, and several polytitanates, such as Ba_2TiO_4, $BaTi_2O_5$, and $BaTiO_7$, were observed at higher annealing temperatures.

Rehspringer [19] prepared $BaTiO_3$ powders by mixing the same ethoxides in the presence of a large excess of alcoholic water (400%). The reaction led to the formation of very fine amorphous powder (~30 nm) 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 temperatures (~ −45 to 0°C). After drying, the gels can be transformed at 725°C into a glassy matrix containing small egg-shaped $BaTiO_3$ crystals.

53.3.1.2. 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 that resulted was separatedby 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 $BaTi_6O_{13}$ (1:6).

53.3.1.3. Preparation Using Ba(OH)$_2$

Flaschen [22] proposed an aqueous synthesis of $BaTiO_3$ by the dropwise addition of tetrapropyl titanate into 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:

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

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

53.3.1.4. Preparation Using Ba-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 to 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 pyrolyzed in air. Crystalline $BaTiO_3$ is noted around 550°C together with $BaCO_3$ and other polytitanates. The power is composed of small plates 10 μm thick made up of clusters of $BaTiO_3$ (~0.5 μm) associated with very small crystallites (20–40 nm).

53.3.1.5. Preparation Using Ba-Acetate and Ti-Alkoxide

This novel method is quite interesting, because 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 [25–27] 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 to 20 cm/min for a sol viscosity of 2.5 to 4 cP. For both products, crystallization starts around 550 to 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 the large-angle X-ray scattering method. They showed that for $T < 250$°C, $Ba_4(HC_3COO)_8$ units are associated to Ti_3 and Ti_6 complex molecules. Pyrolysis of the organic ligands with Ba–O–Ti bonds breaking occurs between 250 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 a $BaCO_3$–TiO_2 reaction. Gels dried hypercritically at 280°C, 200 bars, and analyzed by transmission electron microscopy (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].

53.3.1.6. Another Preparation

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

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

$$\text{b. } H_2[Ti(C_6H_4O_2)_3] + BaCO_3 \xrightarrow[(100^\circ C)]{H_2O} Ba[Ti(C_6H_4O_2)_3] + H_2O + CO_2 \quad (6b)$$

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, >1 hr into a crystalline $BaTiO_3$ fine powder.

53.3.2. Gels, Powders, and Films Characterization

Most of the available characterization of the Ba-titanate-derived materials was obtained by X-ray diffraction and TEM studies. Differences in alkoxide precursor, hydrolysis and polycondensation conditions, and drying and calcination conditions 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 "$BaTiO_3$" intial product is amorphous, but the structure of the chemical complex is not well known; when calcined at 500 to 600°C, it transforms into crystalline $BaTiO_3$ with a 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 in the range of 5 to 10 nm aglomerated in <1-μm clusters and are considered >99.9% pure. Calcination at a higher temperature increases the grains size and the powder density, but no other polytitanates are observed. Figure 53.4 shows as an example TEM micrographies of $BaTiO_3$ powders prepared with the Ba-acetate–Ti-isopropoxide precursor method under different pH and drying conditions; the powders have been later calcined at 700°C during 4 hr. The figure illustrates the complexity and the dependence of the structure on the processing conditions that can have a definite influence on the sintered ceramics microstructure and physical properties.

Interesting dielectric characteristics are obtained after sintering at an elevated temperature, but no systematic study has been done yet to find out the best processing conditions. At this stage the density is close to the theoretical one [16, 17], and the ceramics structure presents virtually no internal and grain boundary porosity [16, 17]. Figure 53.5 shows typical results of ε' and $\tan\delta$ obtained by us, Mazdiyasni and Brown [17], and Martens [32]. The overall behavior is analogous for all systems. Our sintered material has the highest dielectric constant at room temperature, but the Curie point is not as sharp as

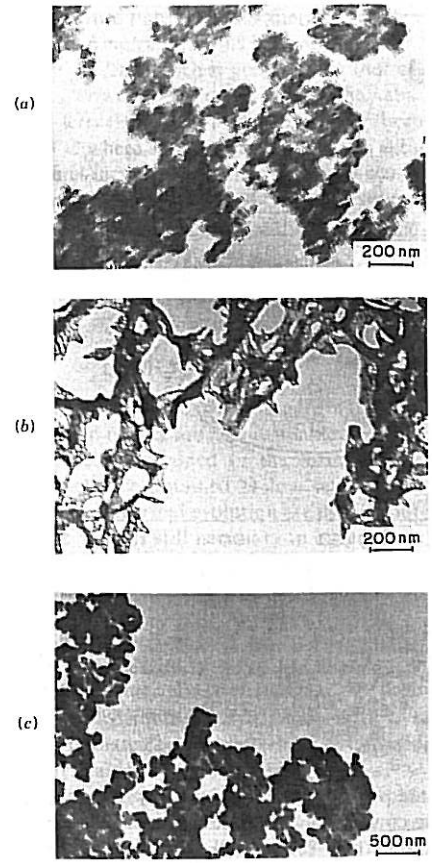


Figure 53.4. $BaTiO_3$ powders structure obtained by the Ba-acetate–Ti-isopropoxide method (see section 53.3.1.5) and calcined at 700°C for 2 hr: (*a*) Sol prepared at pH 4.3 and dried at 100°C; (*b*) sol prepared at pH 9.4 and dried at 100°C; (*c*) sol prepared at pH 4.3 and hypercritically dried at 280°C, 200 bars.

the other two and the maximum value of ε' is lower than that found by Mazdiyasni and Brown. This broadening may be due to the presence of regions with a different T_c, defects that inhibit the domain wall movements, or grain size effects.

The highest Curie temperature of these materials agrees with the value found for a single crystal [33]. The lower value obtained for the Martens material is

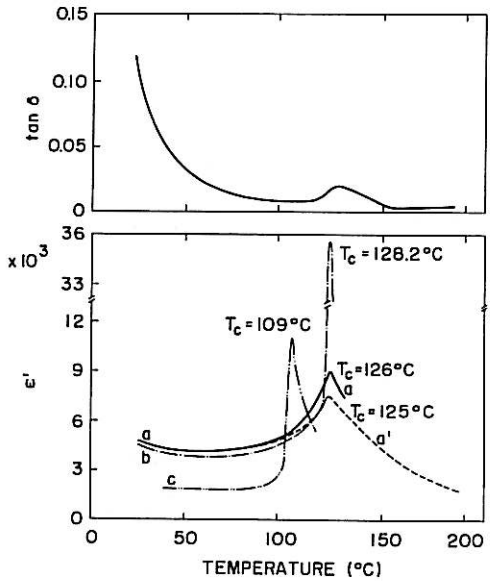


Figure 53.5. The dielectric constant and dissipation factor measured as a function of temperature of pure $BaTiO_3$ ceramics prepared with *a* and *a'*, powder obtained from the Ba-acetate–Ti-isopropoxide mixture (see Section 53.3.1.5) calcined at 700°C and sintered at 1350°C, 2 hr (*a'*) and 5 hr (*a*) ($f = 10$ KHz); *b*, powder obtained from Ba and Ti-alkoxide mixture (see section 53.3.1.1), calcined at 50°C and sintered at 1350°C, 1 hr (data from [17]); *c*, powder obtained by Martens [32] and sintered at 1325°C, 4 hr (precursor preparation and processing not available).

due to the high reported percentage of SrO impurity (2.3 wt %, [32]). Above T_c our measurements are consistent with a Curie-Weiss behavior, $\varepsilon' = C/(T - T_0)$, where $C = 5.3 \times 10^6$°C and $T_0 = 88$°C. In all cases the $\tan\delta$ behavior is normal with a small distontinuity at the Curie point. Phule and Risbud [27] have also reported that the powder calcined at 700°C and sintered at 1350°C for 6 hr have a dielectric constant of 4000.

Until now and in spite of its fundamental technological importance for the preparation of multilayer capacitors, $BaTiO_3$ obtained in thin-film form has been poorly characterized. A dense amorphous single layer 30 to 120 nm thick with an index of refraction $n = 2.0$ can be deposited by the dip-coating technique on glass, α-SiO_2, and metallic substrates. Thick layers can be prepared by repeating the process. According to X-ray diffraction and differential thermal and thermogravimetric results, crystallization into tetragonal $BaTiO_3$ structure occurs in the temperature range 450 to 500°C [23, 25] or 700°C [18]. Annealing

at a higher temperature only increases the grain sizes, and no other titanates have been reported. Amorphous films have an electrical breakdown strength of the order of 9×10^6 V/cm, which is greater than that of crystalline films $\sim 10^5$ V/cm. The values, however, are dependent of the substrate material [18, 23]. Manifestation of ferroelectric properties have only been reported after a heat treatment at 800°C where sufficient a grain size of 0.1 μm has been obtained. Higher temperatures increase the grain size, but is accompanied by film cracking and the formation of cavities. The dielectric response is poor ($\varepsilon' \sim 50$–80), $\tan\delta \sim 2$–3) and shows a broad Curie point at 118°C with little increase of the dielectric constant [18].

53.4. CONCLUSION

Sol–gel processing of lead and barium titanate materials is possible, and various precursor preparation recipes are now available and have been reviewed. These materials can be better obtained in the 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 eluciate these processes.

All the materials crystallized at relatively low temperatures (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 lowers the temperature of formation of pure lead and barium titanate-derived materials, but it is 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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