

## PURE THIN FILMS FROM Ba/Ti ALKOXIDES

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### ABSTRACT

Barium titanate owes its great importance to the fact that its dielectric constant is about 100 times higher than that of conventional dielectric materials provided its compositional and structural purity is extremely high. The value of crystalline BaTiO<sub>3</sub> bodies as used, for instance, in computer elements, magnetic amplifiers, memory device, etc., depends on both the compositional and the structural purity of the BaTiO<sub>3</sub> crystals. This purity will, in turn, depend on the purity of the raw materials used in manufacturing the BaTiO<sub>3</sub> compound and on the particular methods of manufacture which determine the size, homogeneity, and the structural purity of the crystals. This paper reviews the important theoretical considerations, processing techniques and applications related to sol-gel derived thin films.

**Key words** : dielectric constant, homogeneity, the structural purity of the crystals

### 1. INTRODUCTION

The need for miniaturization of electronic components will, certainly continue. It is not a product of man's interest in space, it is another facet of the increased personalized use of electronics and the increased complexity of devices and equipment, and it is responsive to the need for economy. Additionally, advances in system technology in many respects have become materials-limited. This recognized and critical situation has resulted in research and development of improved electronic oxides material<sup>(1)</sup>.

Fundamental understanding of the relation of microstructural effects to the behavior of BaTiO<sub>3</sub> - based thin film is still quite limited when compared with that for ferromagnetic materials.

Several problems experienced with pure BaTiO<sub>3</sub> may be inherent in the material, but other problems just as serious and limiting can be cited of particular concern is the lack of control over the many variables during processing from powder synthesis to final thin films. Of major importance are impurities present in the starting powders or inadvertently introduced during processing and their influence on the properties of ferroelectric thin films. Although the presence of such impurities may not be a priori adverse, it is important to understand their influence on the final properties or to eliminate them completely, if necessary.

Another area of particular importance is the control and understanding of the microstructure of ferroelectric thin films. Although the relation

between macroproperties and microproperties is not always obvious, fine-grained thin films tend to be stronger and to have more uniform physical properties. Thus, an approach which allows beginning with extremely fine powders of high purity, controlling the production of thin films from these powder, and observing the relation between the resultant microstructure and the final properties of the thin films is indicated. Stoichiometric high-purity submicron perovskite powder have long been of interest for the preparation of dense ferroelectric thin film electronic components.

Among the areas of thin film science and technology which are changing most rapidly, which offer the greatest promise for outstanding improvements in both understanding and applications, and which have the most extensive need of contributions from physics and chemistry, the use of sol-gel techniques to prepare materials with novel chemistries, microstructures and properties seems particularly noteworthy. Activity in this area has been increasing at a rapid, almost-explosive rate, with significant developments being reported on a yearly basis.

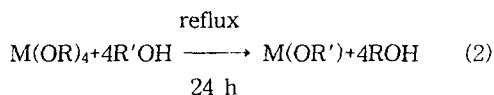
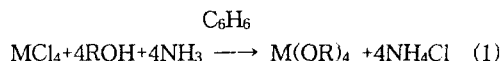
The veritable explosion of interest in this area seems to result in large measure from the perceived technological opportunities. These opportunities include the capability of obtaining fully-dense amorphous solids at temperatures lower by hundreds of Centigrade degrees than those required for conventional compaction/densification or for melting; the possibility of obtaining fully-dense crystalline thin films which cannot be prepared by conventional processing; the ability to obtain materials with novel distributions of phases contained therein; the opportunity of obtaining films with controlled degrees of porosity over wide ranges of porosity ..... the list of possibilities can be extended almost indefinitely.

The present paper will be concerned almost exclusively with the formation of amorphous and crystalline thin films from metal alkoxides.

## 2. EXPERIMENTAL PROCEDURE

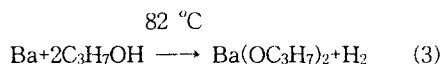
### 2.1. Synthesis of Metal Alkoxides

The Ti alkoxide was synthesized by the method of Bradley<sup>[2]</sup> Mehrotra<sup>[3,4]</sup>, and Brown and Mazdiyasi<sup>[5]</sup>:



where M is Ti and R and R' are isopropyl and n-butyl groups respectively. As-received spectrograde anhydrous 99.5% TiCl<sub>4</sub> was used in preparing these metal alkoxides.

The barium bis isopropoxide was synthesized by the following method:



The 99.9% pure metal shavings were used as-received. Reagent-grade alcohols used in reactions (1) - (3) and all other solvents were dried over a molecular sieve and fractionated at their respective boiling points before use. Typically, 1.1g of recrystallized high-purity barium bis isopropoxide, Ba(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>, and 1.87ml of fractionated titanium butoxide, Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, were dissolved in a mutual solvent such as isopropyl alcohol(C<sub>3</sub>H<sub>7</sub>OH) or benzene (C<sub>6</sub>H<sub>6</sub>). The solution was refluxed for 2h with vigorous stirring.

Taking into consideration the sensitivity of barium and titanium alkoxides towards moisture and CO<sub>2</sub>, all the procedures of preparation of their alcohol solutions were carried out in an atmosphere of dry argon.

### 2.2. Emission Spectrographic Analysis

Table 1. shows the result of the emission spectroscopic analysis of the starting materials, intermediate compounds, and the final oxide product. The increased purity obtained through the successive steps of the preparation of the alkoxides and the decomposition to the oxide is remarkable. Most of the impurities, with the

exception of Si, are eliminated through the synthesis steps. The elements listed do not include all those analyzed for 20 elements but represent those for which the most significant reductions in concentration were observed. None of the unlisted impurities was higher in concentration than those shown in Table 1. for BaTiO<sub>3</sub> after synthesis, nor was any increase over initial impurity content observed during the processing in BaTiO<sub>3</sub>

Thermogramme for the as-prepared alkoxy-derived BaTiO<sub>3</sub> powders are shown in Fig. 1.

The TG of the powders, unwashed and washed with isopropyl alcohol, was run in ambient atmosphere from room temperature to 450 °C. Both types of powder showed an initial 5% weight loss from 70 °C to 110 °C (resulting mostly from loss of alcohol). The additional weight loss observed in this temperature range is attributed to loss of surface-absorbed water.

The isopropanol washing was effective in removing this water, as evidenced by a difference of 15 % in the weight loss in this region. Continued weight loss occurs as the temperature is increased and the remaining carbonaceous material is removed.

The DTA curve for the as-prepared BaTiO<sub>3</sub> powder is also 20% included in Fig. 1.

Dehydration of the powder results in the endotherm observed at 110 °C. The exothermic peak at 340 °C is attributed to the nucleation and growth of the very fine as-prepared particles to larger crystallites. No further peaks were observed on heating to 1000 °C. When the sample was cooled and rerun, no additional peaks were noted, indicating retention of the crystalline phase as formed.

### 2.3. Infrared Absorption Frequencies

The medium infrared characteristic absorption frequencies of stoichiometric high-purity submicron BaTiO<sub>3</sub>, both as-prepared and after calcination at 450 °C for different time intervals, are shown in Fig. 2.

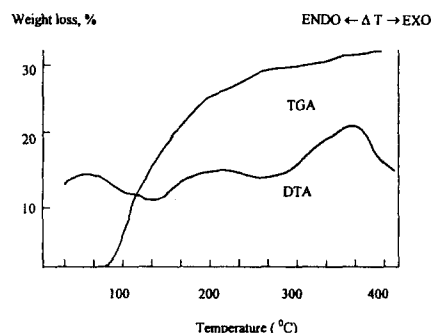
A 3mg sample of the oxide was dispersed in 400mg of anhydrous spectrographic grade CsI

powder and pressed into disks for infrared studies. A Perkin-Elmer model 225 spectrophotometer with interference filter and KBr foreprism was used to cover the region 1000 to 200 cm<sup>-1</sup>.

**Table 1.** Emission Spectrographic Analysis of BaTiO<sub>3</sub> from Barium and Titanium Alkoxides

Elements	Ba (ppm)	TiCl <sub>4</sub> (ppm)	Ba(OPr) <sub>2</sub> (ppm)	Ti(OR) <sub>4</sub> (ppm)	BaTiO <sub>3</sub> (ppm)
Al	80	150	nd<4	nd<5	nd<10
Zr	80	80	nd<5	nd<5	nd<5
Cr	35	nd<3	nd<10	nd<10	nd<10
Sn	100	nd<3	nd<15	nd<10	nd<15
Mn	80	nd<3	nd<30	nd<10	nd<10
Mo	80	nd<3	nd<15	nd<10	nd<10
Cu	30	nd<3	nd<5	nd<10	nd<10
Na	800	300	nd<10	nd<10	nd<10
Mg	50	nd<3	nd<30	nd<3	nd<15
Ni	30	nd<3	nd<3	nd<3	nd<3
Ca	500	100	100	10	100
Sr	700	nd<5	100	100	nd<30
Fe	300	300	nd<10	20	100
Si	50	100	20	nd<10	100

Note: nd = not detected less than



**Fig. 1.** TGA and DTA of Alkoxy-derived BaTiO<sub>3</sub>

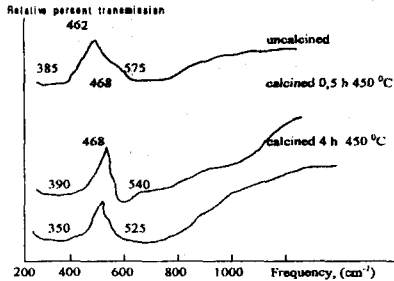


Fig. 2. Medium infrared spectra of calcined and uncalcined BaTiO<sub>3</sub>.

Fig. 2 illustrates the position and intensities of the medium infrared absorption frequencies of the tetragonal BaTiO<sub>3</sub> powder. The bands at 525 to 575 cm<sup>-1</sup> and 350 to 390 cm<sup>-1</sup> are in very good agreement with results reported by Last<sup>[6]</sup> and by Spitzer et al.<sup>[7]</sup> for BaTiO<sub>3</sub> in powder form. Both papers assigned the 525 to 575 cm<sup>-1</sup> band to a normal TiO<sub>6</sub> octahedra vibration mode.

Last, however, interpreted the 350 to 390 cm<sup>-1</sup> band as Ti-O "bending", whereas Spitzer et al. suggest that this absorption is a scattering effect observed only in powdered BaTiO<sub>3</sub>. This interpretation is based on observation of additional absorption bands at 181 and 33.8 cm<sup>-1</sup> in BaTiO<sub>3</sub> single crystals. In any case both the infrared and X-ray diffraction data reported in the present paper agree very well with the identification of crystalline cubic or tetragonal BaTiO<sub>3</sub> as it is synthesised.

#### 2.4. X-Ray Diffraction Studies

The X-ray powder and gel patterns of the material as-prepared after calcining at 450 °C for 30 min and 4 h, using CuK<sub>α</sub> radiation, are shown in Table II; the X-ray diffraction results after 30 min and 4 h are almost identical with the X-ray pattern of the as-prepared powder at 50 °C. A slight shrinkage of the lattice occurs with increased calcination time, an effect consistent with an increase in crystallinity with degree of calcination. All diffraction lines shown for the 4-h material agree well with the 29 ASTM values

for tetragonal BaTiO<sub>3</sub>, but line broadening effects prevent an absolute differentiation between the tetragonal and cubic crystal habits of the material because of the very small c/a ratio. Since a precision lattice parameter determination was not attempted, the fact that the d values is not considered significant.

The 4.355, 3.121, and 3.099 Å lines are easily identified with CuK<sub>α</sub> radiation. The 4.020 and 3.486 Å lines are b unidentified, but twinning at the incomplete calcination stage is a possibility.

Table 2. X-Ray Diffraction Powder Data for Submicron BaTiO<sub>3</sub> (CuK<sub>α</sub> Radiation)

Uncalcined 50°C d (Å)	Calcined 450 °C 30 min d (Å)	Calcined 450 °C 4h d (Å)
4.320 vw	4.353 vw	4.355 vw
4.022 vw	4.020 vw	
3.952 vw	3.970 w	3.978 w
	3.486 vw	
	3.099 vw	3.121 w
2.836 vs	2.814 vs	2.814 vs
2.315 s	2.301 s	2.307 s
2.013 s	1.998 s	1.988 s
1.797 w	1.784 w	1.777 w
1.645 s	1.629 s	1.631 s
1.418 w	1.412 s	1.414 s
1.340 vw	1.328 w	1.331 w
1.230 vw	1.263 s	1.263 s
1.209 vw	1.204 w	1.204 w
1.1715 vw	1.1532 w	1.1538 w
1.1133 vw	1.1072 vw	1.1067 vw
1.0767 w	1.0690 s	1.0685 s

Note: vs = very strong; s = strong; w = weak, and vw = very weak

#### 2.5. The Dip-Coating Technique

It is well known that amorphous and crystalline coatings can be prepared at relatively low temperature using the metal alkoxide sol-gel process. The dip-coating technique makes it possible to coat ceramic and metal substrates with oxide films. In this technique, the substrate is dipped into the metal alkoxide solution, withdrawn vertically, evaporated at room temperature, and heated to several hundred

degrees Celsius. This technique has some valuable characteristics: (1) it is simpler than vacuum evaporation, (2) it is amenable to coating complex shapes, and (3) it improves chemical durability and abrasion resistance, for instance.

In this work, formation of colorless, adherent thin films of  $\text{BaTiO}_3$  was studied. Thickness of the films was determined as a function of the number of dippings, and the structure of the films was determined by SEM, TEM and XRD.

Titanium alkoxide solution containing Ba was prepared by dissolving 1.68 g of Ba in 30 ml  $\text{C}_2\text{H}_5\text{OH}$  and adding 2 ml of  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  to the solution (Ba/Ti mol ratio = 1/1). Aluminum foils were ultrasonically cleaned with an ethanol solution and dried. After the foil was dipped into the solution, it was withdrawn vertically, evaporated at room temperature for 5 min, and heated for 5 min in air at  $450^\circ\text{C}$ . If necessary, these procedures were repeated.

### 3. MEASUREMENT OF PROPERTIES

Thickness of the films was measured as a function of the number of dippings or the concentration of the solutions. The surfaces of the films were observed by scanning electron microscopy SEM. Solutions of Ba/Ti=1/1 were gelled at room temperature by the reaction with moisture in air for 300 days and heat-treated for 3hrs at  $450^\circ\text{C}$ , and the structure was determined by X-ray diffraction (XRD). The films and the gelled and heat-treated sample of Ba/Ti=1/1 were observed by transmission electron microscopy (TEM).

The  $\text{Ba}(\text{OC}_2\text{H}_5)_2$  solution was colorless and transparent. When  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  was added, the color of the solution changed to light-yellow. This solution is called "as-prepared solution".

After the aluminum foil substrate was dipped into this solution, the sample was slightly yellow and transparent or translucent. After the sample was heat-treated for 5 min at  $450^\circ\text{C}$ , the film was colorless and very adherent. Faint rainbow colors that seem to be caused by interference

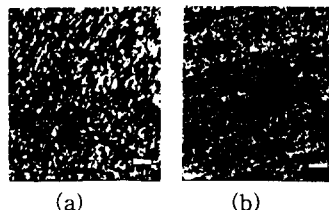


Fig. 3. Microstructures of surfaces of films from (a) as-prepared solution and (b) 24-hrs solution (bar=1 m).

between the boundary of the foil and film and the surface of the film were observed.

When the solution was used after aging for 24hrs (called "24-hrs solution"), the films were translucent and hazier than the films prepared from as-prepared solution, and interferential colors were not observed.

The surface microstructure of the film, particularly surface roughness, is shown in Fig. 3. The surface of the films using as-prepared solution (Fig. 3a.) is of finer texture compared to the surface obtained using the 24-h solution (Fig. 3b.). The reason for this difference in microstructure is likely caused by the difference in the extent of hydrolysis of titanium alkoxide solution. Hydrolysis of titanium alkoxide solution progresses by reaction of the small amount of water in air, and/or  $\text{C}_2\text{H}_5\text{OH}$ .

The solutions were gelled at room temperature and heat-treated at  $450^\circ\text{C}$  for 3hrs, and the solid samples thus obtained were subjected to XRD analysis, shown in Fig. 4.

Since the thickness of the film obtained by one dipping is 200 nm, it was difficult to obtain diffraction patterns using a normal XRD technique. Therefore, the coated film obtained using as-prepared solution was scratched and stripped off, and the structure of the fine powder thus obtained was observed by electron diffraction. Fig. 5 shows TEM micrographs and electron diffractions of (a) the coated film stripped and (b) the solution gelled and heat-treated for 3hrs (both Ba/Ti=1/1).

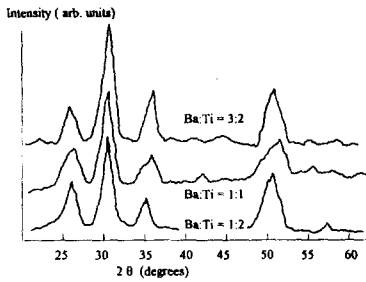


Fig. 4. X-ray diffraction patterns of gelled and heat-treated samples.

In Fig. 5(a), diffraction circles are broader and weaker than ones in Fig. 5 (b), showing that the film is partially crystallized and that the heat-treated gel is crystallized more.

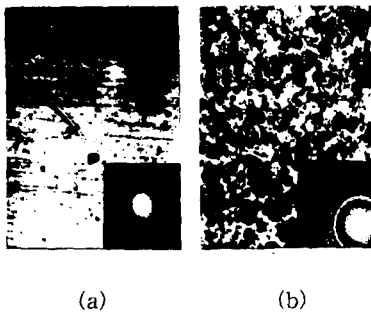


Fig. 5. Transmission electron micrographs and electron diffraction patterns of (a) as-prepared film, (b) gelled and heat-treated solution (bar = 1 μm).

The sol-gel method consists of making a homogeneous solution of the component metal alkoxides in a suitable solvent, usually the parent alcohol, and then causing the hydrolysis under controlled conditions to produce a gel containing the hydrated metal oxide. The gel is then dried, compacted, and fired to produce a crystalline or amorphous material at a temperature much lower than that required by the conventional sintering process. The advantages of the sol-gel process reside in the high purity of the metal alkoxide precursors, the homogeneity of the components at the

molecular level, and the low processing temperature. These features are all of paramount importance in fabricating electronic thin films. A wide range of electronic materials may be deposited by using the sol-gel process, which is a promising technique for forming coatings on glasses, metals, or semiconductors. This technique has the advantages that it is applicable to substrates with large areas and complicated shapes and is relatively simple, and thus low cost. In this paper we shall restrict our coverage to those aspects of the chemistry of metal alkoxides that are particularly relevant to the use of these compounds as precursors for BaTiO<sub>3</sub> films in the electronics industry.

The reason for this difference in microstructure is likely caused by the difference in the extent of hydrolysis of Ti(OR)<sub>4</sub> and Ba(OR)<sub>2</sub> alkoxide solutions. The influence of the following conditions on the quality of the films was studied:

- (a) concentration of the solution;
- (b) 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.

#### 4. CONCLUSIONS

Here we may draw the following conclusions :

1. The coating films using the as-prepared sol appeared more transparent and had stronger dielectric properties compared with the coating obtained from the 24-h sol. Finer texture was observed in the surface of the former by SEM.
2. The electron diffraction analysis showed that the film from "fresh" sol was partially crystallized, and the heat-treated gels from 24-hrs sol were crystallized more.
3. The amount of air moisture, as well as the "age" and types of alkoxides and solvents and also the electrophoresis conditions should be considered to investigate the structure development during the sol-gel transition.

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