Preface

The sol-gel method is known to produce materials from solutions either in bulk, coating films, fibers or powders. It is also known that this method makes low temperature processing of materials possible. This technology has dramatically grown in these two or three decades. The sol-gel method covers optical, electronic and magnetic, chemical, mechanical, biomedical and biotechnological materials. Concerning the microstructures, sol-gel applies to porous materials, dense materials like glasses and ceramics, and organic-inorganic hybrids and nanocomposites. The four volumes of this reference treat four areas that are timely, important and seeing great research activity:

1. **Sol-gel prepared ferroelectrics and related materials.**
2. **Sol-gel processing of titanium oxides: photocatalyst and other applications.**
3. **Sol-gel prepared organic-iorganic hybrids and nanocomposites.**
4. **Sol-gel processing of porous materials: application to catalysts, enzymes, chemical analysis, sensors, and membranes.**

The goal of these four volumes is to disseminate the recent research results published in recent issues of *Journal of Sol-Gel Science and Technology*, which is a unique journal devoted to Sol-Gel. Papers have been selected from those published in volumes 16 -25 of the *Journal of Sol-Gel Science and Technology* spanning the years 1999-2002.

Volume 1 presents papers on preparation, structure, properties and applications of ferroelectrics and related materials, such as, piezoelectric and pyroelectric materials . Hereafter, these materials will be abbreviated as ferroelectric materials. Representative ferroelectric materials include $BaTiO_3$, $Pb(Ti,Zr)O_3$, $PbTiO_3$, $LiNbO_3$, $KNbO_3$, $LiTaO_3$, and $Pb(ZnNb)O_3$.

   Generally, these materials have a high dielectric constant and are characterized by large piezoelectric, pyroelectric and electrooptic effects as well as nonlinear optical effects. On the basis of these unique properties, ferroelectric materials have been applied to produce active elememts of various devices. Due to a high dielectric constant, ferroelectric materials are utilized to produce high capacity condensers. Piezoelectric materials are used to produce piezoelectric transducers, oscillators, transformers, surface acoustic wave devices and actuators. Pyroelectic materials are used in sensor devices for detecting infrared rays such as temperature sensors.

   Recently, thin coating films emerged as a new, important form of ferroelectric materials. Thin films are especially useful in micro-devices. So far, most of the thin films of ferroelectric materials have been produced via gas phase deposition methods. Since about ten years ago, material scientists noticed that sol-gel processing easily provides coating films of oxides on various substances including platinum-coated silicon semiconductors and MgO and Al_2O_3 substrates. Multi-layered as well as mono-layered films can be prepared by the sol-gel method. Thin film formation can be applied to new ferroelectric mateials, such as $SrBiTa_2O_9$, which proves suitable for non-volatile random access memory devices.

The subjects of the papers collected in this volume cover a wide range of aspects of sol-gel ferroelectric materials: formation, structure, properties and applications. More than 60 % of the papers deal with coating films, which may indicate the present and future direction of sol-gel dielectric materials.

Volume 2 contains papers on sol-gel processing of titanium oxides for photocatalyst and other recent applications. Titanium dioxide, TiO_2, is both an old and new material with a variety of interesting functions. Conventionally, TiO_2 was used mainly as light-scattering particles in porcelain enamel, ceramic glaze, white points and the suspension-type eraser. Its high covering ability based on the high refractive index gives objects their white appearance. A more recent application of similar nature is the incorporation of TiO_2 into UV- shielding cosmetics, which protect human skin from UV damage. TiO_2 is also employed as nucleating agent for crystallization of glass, providing glass-ceramics.

In the 1990s, application of TiO_2 to photocatalysts, solar cells and reflective and non-reflective coatings have been extensively studied. The most popular application of TiO_2 is in the photocatalysts, which oxidize or decompose organic matter and nitrogen oxide upon UV-irradiation, thus creating a self-cleaning environment. It is interesting to see that all the applications mentioned above mainly use TiO_2 in a form of a coating film.

This means that the sol-gel processing is suitable for preparing TiO_2 for photocatalysts. Solar cells should be porous, in order to absorb UV lights or sun lights. In this case, too, sol-gel processing is suitable.

The collection of research papers on TiO_2 should very much benefit people engaged in materials related technology. Since the microstructure is important in applications of TiO_2, the papers concerning the basic study on the relation of synthesis parameters to microstructure are also included.

Papers on sol-gel prepared organic-inorganic hybrids and nanocomposites are compiled in **Volume 3**. Typical organic-inorganic hybrids have a microstructure in which inorganic species like -Si-O-Ti-O- are combined with organic polymers like polymethylmethacrylate chains at the molecular level. Ormosils (Organically modified Silicates) and Ormocers (Organically Modified Ceramics) are one of the hybrids. Organic-inorganic nanocomposites have a microstructure in which organic (inorganic) nanosized particles are dispersed in inorganic (organic) matrices, having chemical connections. Because of the combination of organic species to inorganic species, hybrid materials are characterized by higher resistance than the organic part, by higher flexibility than the inorganic part, and by higher strength of the gel than that of the inorganic gel. Nanocomposites possess color, luminescence, nonlinear optical properties and other functional properties.

The sol-gel method is very important for organic-inorganic hybrids and nanocomposites, because it may be the only powerful method for preparing these materials. Because of the presence of organic matter in these materials, the synthesis has to be done at low temperatures. For this reason, organic-inorganic materials have been attracting much attention and are now a very popular subject among people interested in sol-gel preparation of materials.

The papers collected in this volume cover a broad area of organic-inorganic hybrids and nanocomposites including types, processing, properties and applications of the materials.

Volume 4 compiles papers on the gel as porous material. Porous gels with nano-size pores and micron-size pores are applied to formation of catalysts, enzymes, chemical analysis, sensors and membranes. Pore surfaces are significant because they serve as the absorption and reaction site for catalysts, enzymes, chemical reaction, and sensing molecules or atoms.

The oxide gels, such as silica, titania, zirconia, and alumina, are usually highly porous, which means that the sol-gel method is suitable for producing porous materials, catalysts and catalyst supports. Accordingly, the sol-gel method has attracted much attention as a method of making porous materials.

Many papers have been published on the control of the porosity, size and size distribution of pores and on the morphology and arrangement of pores. Drying gels under supercritical conditions produces aerogels with very high pore contents. Simultaneous occurrence of phase separation and gelation in alkoxysilane solutions containing water-soluble organic molecules produces micron-size connected pores among micron-size particles containing mesopores. Self-organization taking place in gelling solution containing surfactants and alkoxysilanes produces coating films in which cylindrical mesopores are preferentially oriented. It is known that many factors in sol-gel processing affect the porous structure of the gel.

The papers in these four volumes cover a wide range of topics in the sol-gel area. It is hoped that by organizing this material into these topical volumes that we have created a useful reference for researchers and students interested in the sol-gel method.

Preparation and Characterization of (Ba,Ca)(Ti,Zr)O$_3$ Thin Films Through Sol-Gel Processing

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Abstract. $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ thin films were prepared from Ba-Ti and Ca-Zr precursors by sol-gel processing. Polymerizable solutions containing Ba-Ti and Ca-Zr, respectively, were newly synthesized. Decomposition of the starting compounds and crystallization behavior of the film were examined by using TG/DTA and XRD. Microstructure of thin films was observed by using SEM. Polycrystalline $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ films obtained by firing at 800°C were dense with fine grains. The thin films showed a dielectric constant of 1200 and dielectric loss of 0.5%.

Keywords: sol-gel, (Ba,Ca)(Ti,Zr)O$_3$, thin films, dielectric constant, dielectric loss

1. Introduction

Sol-gel processing is one of the promising methods to prepare well-defined ferroelectric films at relatively low temperatures. Recently, high quality ferroelectric thin films have been extensively applied to various devices including capacitors, sensors, nonvolatile memory devices and microwave communication devices. Among various methods of fabricating thin films such as liquid phase epitaxial growth (LPE), chemical vapor deposition (CVD), sputtering, laser ablation and sol-gel processing, the sol-gel processing is characterized by low temperature preparation leading to thin films of good homogeneity, high purity and controlled chemical composition.

Recently a great many number of multilayer ceramic capacitors are used in electronic devices, because it has become possible to produce multilayer ceramic capacitors of small size of 0.5 × 0.5 × 1.0 mm or 0.3 × 0.3 × 0.6 mm. These multilayer ceramic capacitors are used as chip capacitors and are manufactured by tape-casting, screen-printing, and laminating processes. However, much smaller size capacitors, such as thin film capacitors, are required for electronic equip-

ments. In this case, the conventional method will not work any more. Thin film capacitors can fulfil the demand by increasing the dielectric constant of the materials used in the capacitor or by decreasing the thickness of the dielectric layer. For some applications it is useful to apply the capacitor directly to the integrated circuit as a thin film. The sol-gel processing is a feasible way to fabricate such thin film capacitors [1–5], owing to the advantages mentioned above.

(Ba,Ca)(Ti,Zr)O$_3$ ceramics are assumed to satisfy the dielectric properties needed for thin film capacitors. Since the discovery in 1955 by McQuarrie [6], (Ba,Ca)(Ti,Zr)O$_3$ has been extensively studied on its ferroelectric properties. In recent years, most of the studies have been concentrated on powders. Only a few papers have reported on the preparation of BaTiO$_3$ based materials for multilayer ceramic capacitor by solid chemical processes [7]. There have been no report on thin films of the (Ba,Ca)(Ti,Zr)O$_3$ system prepared by sol-gel method, sputtering and chemical vapor deposition.

This paper discusses the crystallization and characterization of (Ba,Ca)(Ti,Zr)O$_3$ thin films prepared from newly developed precursors. The objectives of this study are (1) to develop alkoxide-based solution systems for Ba-Ti and Ca-Zr, and thin films with

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compositions in the Ba-Ca-Ti-Zr system, and (2) to investigate processing and properties of resultant ferroelectric thin films.

2. Experimental

2.1. Preparation of Alkoxide Solution

New procedure was developed specifically for the Ba-Ti and Ca-Zr systems. All alkoxide-based solutions were sensitive to air and moisture, so were prepared under flowing nitrogen or vacuum conditions.

Barium ethoxide, titanium isopropoxide (Kojundo Chemical Laboratory Co., Ltd.) and solvent 2-methoxyethanol were selected. The synthesis of Ba-Ti solution is summarized in Fig. 1(a). Two precursor

Figure 2. Synthesis of Ba-Ca-Ti-Zr complex alkoxide solution.

solutions were prepared: (i) a Ba precursor (Ba-methoxyethoxide) and (ii) a Ti precursor (Ti-methoxyethoxide) solution. Ba and Ti precursors were combined in a 1 : 1 molar ratio, dissolved in 2-methoxyethanol, and heated. Volatiles were removed by distillation until the temperature of 2-methoxyethanol with condensing vapors reached 125°C boiling point in nitrogen atmosphere. The solution was then diluted with 2-methoxyethanol, and the distillation was repeated twice. During the final distillation, the Ba-Ti precursor solution was concentrated to approximately 1 M, based on Ba content.

Fig. 1(b) shows the preparation procedure for Ca-Zr alkoxide-based solution. Ca and Zr precursors were prepared from Ca and Zr ethoxide (Kojundo Chemical Laboratory Co., Ltd.) and 2-methoxyethanol, respectively. Ca and Zr precursors were combined in a 1 : 1 molar ratio, refluxed in excess 2-methoxyethanol, heated, and distilled twice in nitrogen atmosphere.

The two precursor solutions (Ba-Ti and Ca-Zr) were mixed in a 0.92 : 0.08 molar ratio at room temperature, reacted at 128°C and concentrated by distillation (Fig. 2). Using a procedure identical to that described for Ba-Ca-Ti-Zr solution, three successive dilutions and vacuum distillations were used to remove reaction by-products and prepare a stable solution. The volume of the final solution was adjusted to give a 1 M Ba-Ca-Ti-Zr stock solution, based on Ba content.

2.2. Preparation of Thin Films

Platinized Si substrates, Pt/Ti/SiO$_2$/Si, were used after degreasing in acetone and 2-methoxyethanol with

Figure 1. (a) Synthesis of Ba-Ti alkoxide-based solution; (b) Synthesis of Ca-Zr alkoxide-based solution.

ultrasonic. A multilayered spin coating techniques was used for preparing thin films. In order to obtain uniform layers with a minimum number of visible defects, the conditions for spin coating were optimized. Immediately prior to the solution deposition, substrates were cleaned with deionized water, blown-dry with filtered N_2, and dried on a hot plate. The precursor solution was syringed through a filter (0.2 μm) onto the substrate, and spinning was started immediately. The deposition conditions were the same for all samples (3000 rpm and 30 s). After each deposition, the samples were heat-treated on a hot plate to remove residual solvents. Each coating produced a film of about 50–70 nm in thickness. The deposition and heat-treatment were repeated to prepare a thicker coating film. Depending on the temperature of the heat-treatment, a further heating was sometimes necessary, in order to crystallize the thin films. The firing profile for this heating was set to start at a rate of 200°C/h up to temperature 800°C and then maintain at this temperature for 1 h.

Thin films capacitors were fabricated by sputtering aluminum as the top electrode of the layer surface. The dielectric layer was sandwiched between the aluminum and the platinum layer, which served as the bottom electrode. The top electrode (2 mm ϕ) layer was patterned by using a mask.

2.3. Characterization of Ba-Ca-Ti-Zr Thin Films

The elemental composition of the solution was determined by inductively coupled plasma emission (ICP). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Rigaku, TG8120) were used to characterize the crystallization temperatures and the organic decomposition temperatures of organic residues.

The structural investigation was performed on an X-ray diffractometer (RAD-2B, Rigaku). The dielectric properties were measured by an HP4284A LCR meter. The examination of morphology was performed on a scanning electron microscope (Hitachi S-4100).

3. Results and Discussions

3.1. Ba-Ca-Ti-Zr Solution

The synthesis of the Ba-Ca-Ti-Zr alkoxide-based solution required the preparation of two precursors: (i) Ba-Ti alkoxide solution and (ii) Ca-Zr alkoxide solution.

Table 1. Chemical analysis by inductively coupled plasma emission.

Composition	Weight percent				Molar ratio	
	Ba	Ca	Ti	Zr	Ca/Ba	Zr/Ti
Ba-Ca-Ti-Zr	68.0	0.24	23.5	0.46	0.0206	0.0203

During the processing, each precursor reacted in the alcohol to form a heterometallic alkoxide.

Analysis data are listed in Table 1. Ba-Ca-Ti-Zr compositions analyzed are very close to the expected stoichiometry.

3.2. Thermal Evolution of Thermal Gel Powders

For the preparation of ceramics powders, the amorphous metallo-organic gel must be heat-treated to pyrolysis the organic components for crystallization. Fig. 3 illustrates TGA and DTA curves for dried gel powder. In the methoxyethoxide gel powders (Fig. 3(a)), decomposition occurs at approximately 630°C, as revealed by the large exotherm associated with a weight loss. The result for Ba and Ca ethoxide gel powders (Fig. 3(b) and (c)) show similar behavior, although organic decomposition of organic residues occurs at slightly higher temperatures (approximately 660°C for both ethoxides). Crystallization occurs at 740°C for the methoxyethoxide powder, approximately 730°C for the Ba ethoxide powder and at 800°C for the Ca ethoxide powder. Although decomposition of organic occurs at high temperatures for all the gel powders, it should be noted that the magnitude of the weight loss for the ethoxide precursors was less than that for the methoxyethoxide precursor. Since weight loss due to decomposition of organic residues continues up to the crystallization temperature, significant densification prior to crystallization may be impossible.

3.3. Characterization of Thin Films

The barium calcium zirconium titanate films of the [$(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ composition], after firing had a very smooth surface and showed a perovskite single phase. Fig. 4 illustrates the X-ray diffraction patterns for a Ba-Ca-Ti-Zr gel heat-treated for one hour at 800°C (a) and 750°C (b). It is seen that perovskite phase crystals are found in barium calcium zirconium titanate films formed on Si substrate at 750 and 800°C. A detailed examination of the peaks indicated that the
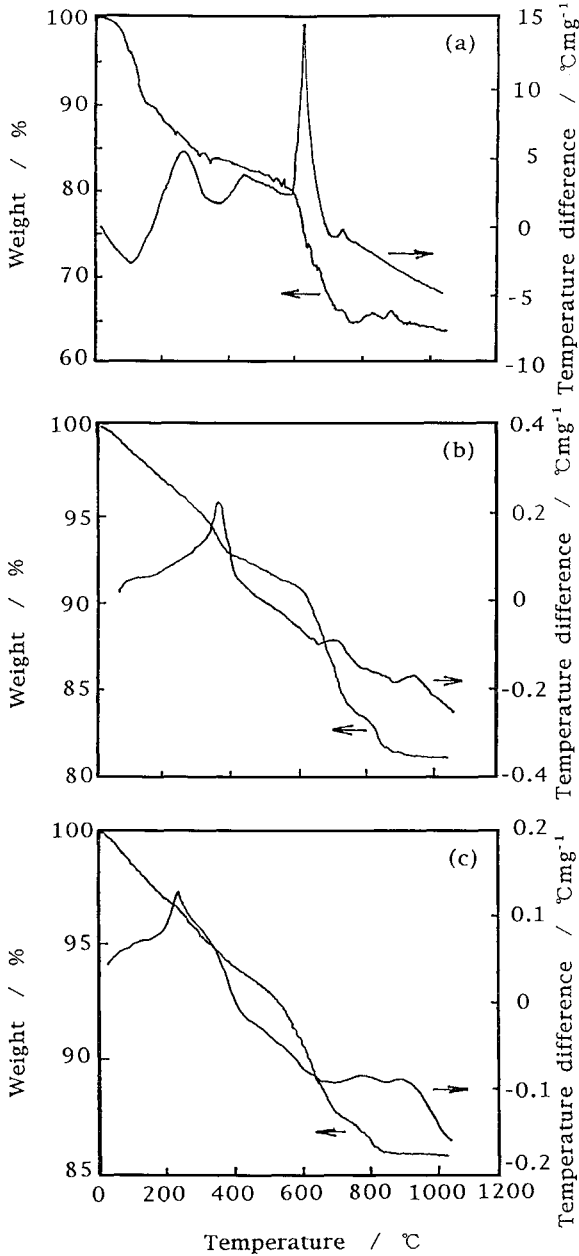
Figure 3. TGA/DTA of dried gel powders (a) Ba-Ca-Ti-Zr methoxyethoxide precursor; (b) Ba ethoxide precursor; (c) Ca ethoxide precursor.

full width at half maximum of the X-ray diffraction peaks decreases when the firing temperature increases from 750 to 800°C. This indicates that the perovskite crystals grow at these temperatures.

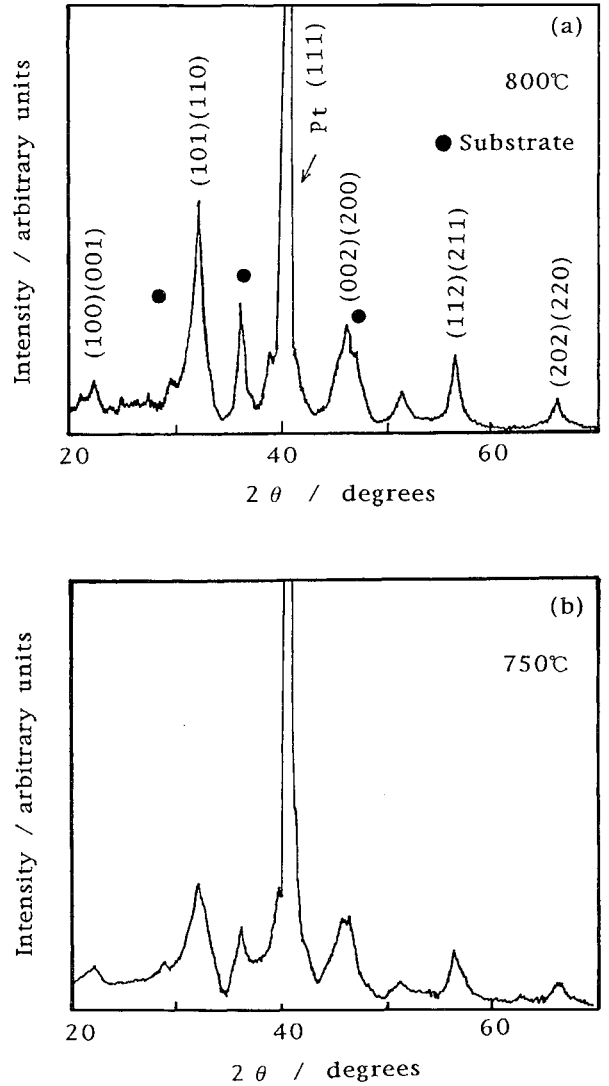Fig. 5 shows the SEM micrograph of the surface and the cross sectional view of barium calcium zirconium

Figure 4. XRD profiles of $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ thin films on platinized Si substrate heat-treated 750 and 800°C for 1 h in air.

titanate, $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$, thin films prepared by heating the gel film with 10 successive depositions at 800°C. The thickness of the film is about 0.6 μm. The grain size of the film heat-treated at 800°C is estimated to be around 0.3 μm and is uniform. This indicates that two or three grains constitute the thickness of the film. The grains were sphere or rod-like on platinized Si substrate. Heat-treatment was necessary after each deposition on a hot plate to obtain a dense microstructure. Layers could be heat-treated without cracking when the aforementioned firing program was used. The uniform grain in thin films suggests that a
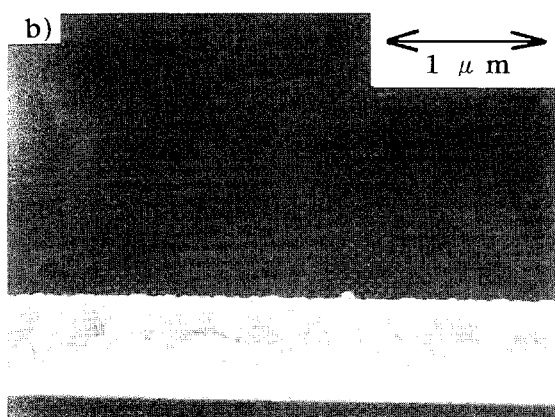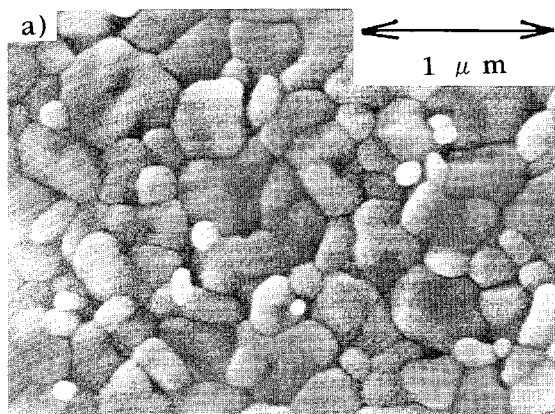
Figure 5. SEM photomicrographs of $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})$ O_3 thin films prepared from Ba-Ca-Ti-Zr complex alkoxide solution. (a) Morphology of the surface of $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})$ O_3 thin films fired at 800°C; (b) Morphology of the cross section of $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ thin films fired at 800°C.

Figure 6. Frequency dependence of dielectric constant ε and loss tan δ for $(Ba_{0.92},Ca_{0.08})(Ti_{0.92},Zr_{0.08})O_3$ thin films.

similar nucleation step worked for all these sol-gel derived materials.

3.4. Dielectric Properties

The value of dielectric constant ε and dielectric loss tan δ at 1 kHz, 100 mVrms, 25°C, for $(Ba_{0.92},Ca_{0.08})$ $(Ti_{0.92},Zr_{0.08})O_3$ thin films heat-treated at 800°C were 1200 and 0.5%, respectively.

Fig. 6 shows the frequency dependence of dielectric constant in the range 100 Hz to 300 kHz. The dielectric constant tends to decrease slightly with frequency. An increase in tan δ values is noted below 100 Hz and above 300 kHz. The behavior at lower frequencies
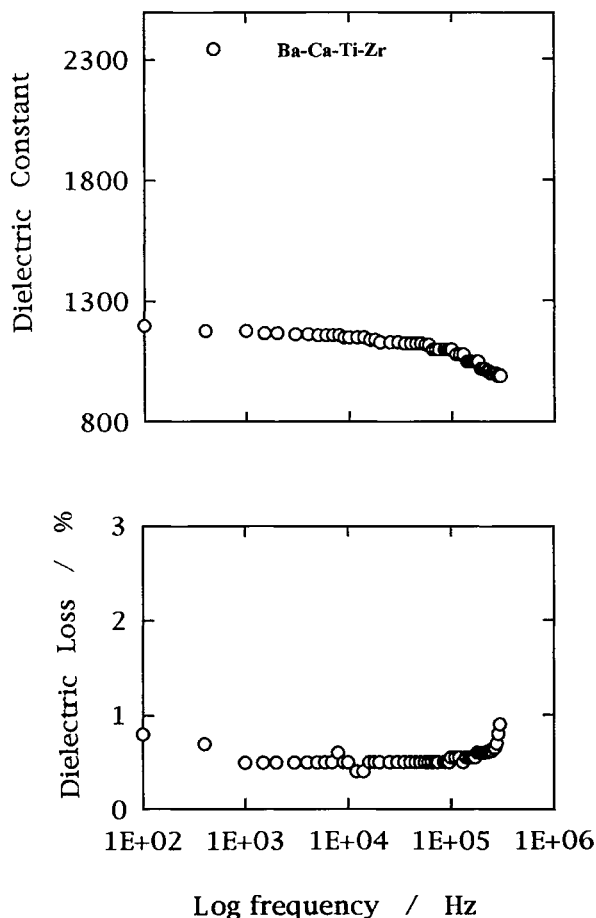
could be due to parallel leakage or interfacial effects and at the upper frequencies, the LCR resonance of the impedance analyzer affected the measurements.

The apparent dielectric constant increased with the thickness of the film as shown in Fig. 7 for Ba-Ca-Ti-Zr thin films. Samples to measure dielectric constant were prepared with 5–13 coatings and heat-treatment at 800°C between successive solution depositions. All specimens had perovskite phase by XRD analysis, and for a given thickness had a higher dielectric constant. The microstructures were not influenced much by the film thickness; the film of 5 coatings had approximately the same grain size as that of 13 coatings. Therefore, the change in dielectric constant with thickness could not be attributed to the grain size. Thickness dependent properties have been reported for thin dielectric and have been attributed to a number of effects, including Shottkey barrier formation [8], change in
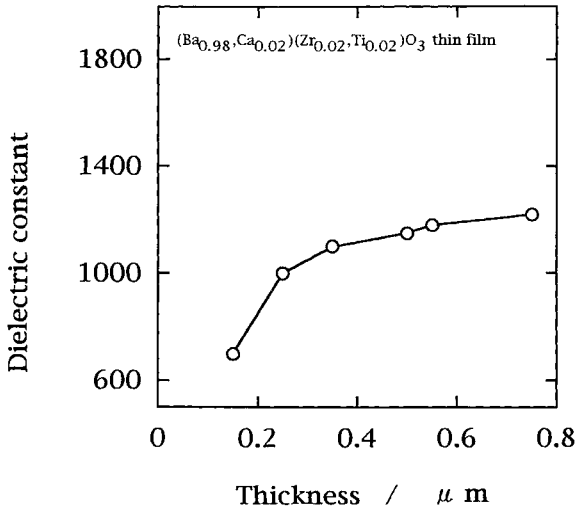
Figure 7. Effect of thickness on dielectric constant for (Ba$_{0.92}$, Ca$_{0.08}$)(Ti$_{0.92}$,Zr$_{0.08}$)O$_3$ thin films.

Figure 8. Current-voltage relationship (*V-I* curve) of (Ba$_{0.92}$, Ca$_{0.08}$)(Ti$_{0.92}$,Zr$_{0.08}$)O$_3$ thin films fired at 800°C on platinized Si substrate.

grain size [9], and density and grain growth variations [10]. These theories have been developed to explain the behavior of evaporated thin films. The stress is also expected to influence dielectric properties. For sol-gel derived Ba-Ca-Ti-Zr film, the thickness dependence may be due to thin, low dielectric constant interfacial layer.

Fig. 8 shows *V-I* characteristics of (Ba$_{0.92}$,Ca$_{0.08}$)(Ti$_{0.92}$,Zr$_{0.08}$)O$_3$ thin films. Optimum values of the nonlinear coefficient obtained for the *V-I* characteristics followed $\alpha = 0.92$, indicating that (Ba$_{0.92}$, Ca$_{0.08}$)(Ti$_{0.92}$,Zr$_{0.08}$)O$_3$ thin films are in ohmic contact with the electrode. The dielectric breakdown voltage was sufficiently high, $V_b = 980$ V.

4. Summary

Thin film dielectrics in the (Ba$_{0.92}$,Ca$_{0.08}$)(Ti$_{0.92}$, Zr$_{0.08}$)O$_3$ system for thin film capacitor were prepared by sol-gel processing. Methoxyethoxide precursor can be used to produce polycrystalline, randomly oriented, fine grain (0.2–0.5 μm) homogeneous perovskite phase thin films on platinized Si substrate by the heat-treatment at 800°C for 1 h. The thin films of single phase perovskite had very good characteristics, dielectric constant of 1200, dielectric loss of
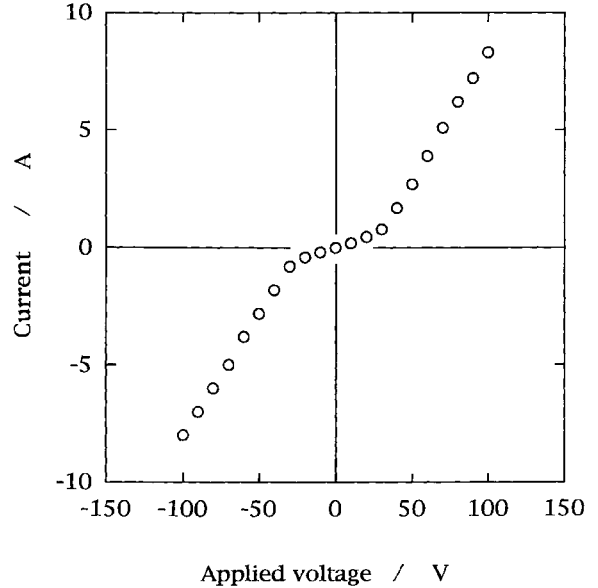
0.5%, nonlinear coefficient $\alpha = 0.92$, and break-down voltage = 980 V. This material has shown promise as dielectric thin film in capacitor.

References

1. N.D.S. Mohallem and M.A. Aegerter, Proceedings of MRS Spring Meeting, Better Ceramics Through Chemistry III. **21**, 515 (1988).
2. M.N. Kamalasanan, S. Chandra, P.C. Joshi, and A. Mansingh, Appl. Phys. Lett. **59**(27), 3547 (1991).
3. K.A. Vorotilov, E.V. Orlova, V.I. Petrovsky, M.I. Yanovskaja, S.A. Ivanov, E.P. Turevskaya, and N. Ya. Turova, Ferroelectrics **123**, 261 (1991).
4. Z. Xu, H.K. Chae, M.H. Frey, and D.A. Payne, Proceedings of MRS Spring Meeting, Better Ceramics Through Chemistry V. **271**, 339 (1992).
5. Y. Xu and J.D. Mackenzie, Integrated Ferroelectrics **1**, 17 (1992).
6. M. McQuarrie, J. Am. Ceram. Soc. **38**(12), 444 (1955).
7. T. Nomura, N. Kawano, J. Yamamatsu, T. Arashi, Y. Nakano, and A. Sato, Jpn. J. Appl. Phys. **34**, 5389 (1995).
8. J.R. Slack and J.C. Burfoot, J. Phys. C: Solid St. Phys. **4**, 898 (1971).
9. S.B. Desu, C.H. Peng, L, Kammerdiner, and P.J. Schuele, Mat. Res. Symp. Proc. **200**, 319 (1990).
10. T. Nakagawa, J. Yamaguchi, T. Usuki, Y. Matsui, M. Okuyama, and Y. Hamakawa, Jpn. J. Appl. Phys. **18**(5), 897 (1979).