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Metallo-Organic Solution Deposition of Ferroelectric PZT Films

Prepared by

R. A. LIPELES and M. S. LEUNG
Electronics Technology Center
Technology Operations

and

D. J. COLEMAN
Mechanics and Materials Technology Center
Technology Operations

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SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
Los Angeles Air Force Base
P. O. Box 92960
Los Angeles, CA 90009-2960

Engineering and Technology Group

THE AEROSPACE CORPORATION
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QUANG BUI, Lt, USAF
MOIE Program Manager



MARK W. BORDEN, Captain, USAF
SSUSI/SSULI Project Officer
DMSP Program Office

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The metallo-organic solution deposition [(MOSD) or sol-gel] technique can be used for preparing lead zirconate titanate (PZT) ceramics with a wide range of compositions and crystal structures for electro-optical applications. Film morphology is affected by stoichiometry of the film, hydrolysis and polymerization of the sol-gel solution, and thermal treatment of the deposited material. The lattice parameter decreases with the amount of titanium in PZT in agreement with ceramic data. A slight initial excess of lead in the coating solution is found to improve film morphology. Unlike traditional powder ceramic processing techniques, MOSD permits the growth of small uniform grains that are conducive to achieving consistent electronic and optical properties. Our results show that the properties of films prepared by the MOSD process can be tailored to meet the needs of device applications.					
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I. INTRODUCTION

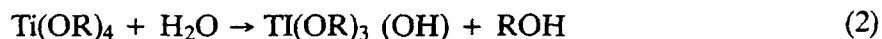
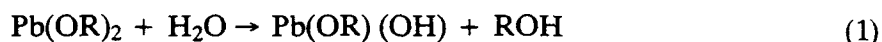
Ferroelectric films are being investigated for use in optical waveguides [1-3], optical switches [3-5], surface acoustic wave transducers [6], and nonvolatile ferroelectric memories [7]. Films for these applications must have reproducible, homogeneous electronic and electro-optical properties. These properties can be obtained in ferroelectric films deposited by metallo-organic solution deposition [(MOSD) or sol-gel] processing. MOSD is a solution-based deposition method where soluble metallo-organic compounds are intimately mixed and polymerized to yield a viscous coating solution. Metallo-organic compounds consist of a central metal atom bonded to organic ligands by oxygen. The solution is used to form a dried, gelatinous film on the substrate by a number of different coating techniques. Ceramic films with a narrow distribution of either microscopic (less than 10 nm) or macroscopic sized grains can be grown from the amorphous film, depending on the thermal processing conditions.

MOSD processing has been applied to a number of different materials, ranging from amorphous glasses to highly crystalline films [8]. In this report, we present the results of our work on the MOSD processing of ceramic lead zirconate titanate (PZT) films. The lanthanum-containing transparent ceramic, lead lanthanum zirconate titanate (PLZT), is an important ferroelectric material for electronic and electro-optical applications. In the PLZT solid solution system, the crystal structure and the electro-optical properties can be tailored for a particular application by changing the stoichiometry [9]. Unlike the lanthanum-free PZT ceramics made from powders, which are translucent or opaque, PZT films are transparent. The challenge in making these PZT films lies in simultaneously obtaining uniform composition, the proper crystal structure, and small grain for low light scattering.

The MOSD processing of films in the PLZT system has been studied extensively. The mixing and reaction of precursors in solution, drying and consolidation, and annealing steps are critical in obtaining dense, optically transparent, ferroelectric films [10-17]. A related solution technique, metallo-organic deposition, uses long-chained carboxylic acid salts to make similar films [18]. In this report, the effects of the solution composition, hydrolysis, and thermal processing on the film morphology, phase segregation, and ease of annealing will be addressed to show the advantages of the MOSD technique.

II. MOSD SOLUTION REACTIONS

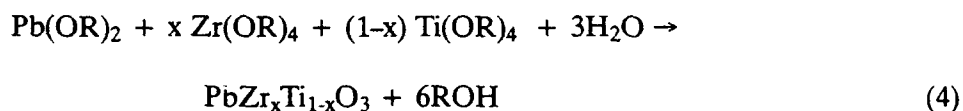
In the MOSD process, metal alkoxides and metal carboxylic acid salts are mixed in solution. These carbon-oxygen-metal bonded metallo-organic compounds are reacted with water to form a metal-oxygen-metal bonded polymer in solution [19]. Polymerization increases the viscosity needed to control the thickness and drying rate of the films. For example, lead alkoxide and titanium alkoxide compounds can be hydrolyzed to form hydroxide-alkoxide compounds:



The alkoxide-hydroxides can react to form the metal-oxygen-metal polymer linkages:



Zirconium alkoxides hydrolyze and react with lead through similar reactions. Further hydrolysis and polymerization can occur, resulting in the polymer precursor for PZT in solution. The complete reaction of the starting materials with water to form $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, where $(0 \leq x \leq 1)$, is:



The amount of water added to the solution is expressed as a molar ratio of water concentration to the total concentration of metals:

$$h = [\text{H}_2\text{O}]/([\text{Pb}] + [\text{Zr}] + [\text{Ti}]) \quad (5)$$

From Eqs. 4 and 5, $h = 1.5$ corresponds to the stoichiometric amount of water for complete reaction. Polymerization of the precursors increases the viscosity of the solution so that it can be coated on substrates by spinning, dipping, or spraying.

III. EXPERIMENTAL

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ films with compositions specified by $(x:1 - x)$, where $0 \leq x \leq 1$, were prepared from stoichiometric solutions of metallo-organic precursors [15-17]. Lead 2-ethylhexanoate, zirconium tetrapropoxide, and titanium tetrabutoxide (obtained from Alpha/Ventron) were mixed in isopropanol to form a solution that was about 0.05 M with respect to PZT. After addition of water for hydrolysis and refluxing for about 1 h, the solution was spun on fused silica or platinum substrates. Three-stage thermal processing in air (consisting of drying, consolidation, and annealing steps) was needed to avoid premature crystallization and growth of large, coarse grains. During thermal processing, the film was dried at 100°C to remove the solvent; it was then consolidated at 300°C to remove most of the other organics. The result was the formation of a dense, amorphous film. The coating, drying, and consolidating steps were repeated six to eight times to deposit an amorphous film. The film was then annealed at 525°C to initiate crystallization of small, uniform grains to preserve transparency of the 600-800 nm thick films. Diffuse light scattering was measured at a wavelength of 632.8 nm from samples deposited on fused silica substrates to characterize the optical quality of the films.

IV. RESULTS AND DISCUSSION

A. HYDROLYSIS AND CRYSTALLINITY

Reaction of precursors in the solution, the composition of the PZT, and thermal processing conditions are major factors in determining film crystallinity and morphology. Crystalline, perovskite structure is necessary for ferroelectricity in PZT films. First, we showed that partial reaction of precursors in the solution was more effective in producing crystalline PZT than complete reaction of the precursors with water. This observation was made on rhombohedral phase PZT at a ratio of Zr:Ti of 0.55:0.45. The effect of hydrolysis and polymerization of the precursors on crystallization during thermal processing was studied using Fourier transform infra-red (FTIR) spectroscopy. Crystallization of the gel resulted in the emergence of a new vibrational band at 540 cm^{-1} , assigned to the vibration of metal-oxygen octahedra in the perovskite lattice [20,21]. The intensity in this band was proportional to the amount of crystallization taking place during annealing of the amorphous gel. In Figure 1, the band at 540 cm^{-1} is larger for $h = 0$ and $h = 0.5$ than for the fully reacted sample ($h = 1.5$). The morphology of these films is shown in Figure 2. The porous structure obtained for $h = 1.5$ indicates that extensive reaction of the precursors formed highly cross-linked and amorphous polymers that were resistant to densification during annealing at 525°C . At lower water concentrations, the amount of cross linking was reduced. As a result, the oligomers formed were more flexible and more conducive to densification than the highly polymerized solution precursors. Our results indeed showed that complete reaction ($h = 1.5$) resulted in porous films and that less polymerization of the precursors ($h = 0$ and $h = 0.5$) increased the crystallinity of MOSD films at lower temperature.

The crystallinity of films prepared from solutions with moderate amounts of water ($h = 0.5$) was compared to the crystallinity of films prepared from dry solutions ($h = 0$). Lead titanate (PT) films were cast on platinum substrates from dry ($h = 0$) or partially hydrolyzed ($h = 0.5$) solutions and were consolidated at 300°C . After deposition of six layers, the films were annealed at either 550 or 600°C . X-ray diffraction was used to measure the intensity of the (110) PZT peak for films listed in Table 1. The peak intensity was proportional to the amount of crystallization in the PZT films. The peak intensities were normalized to the peak intensity of the film annealed at 600°C for 30 min.

The results in Table 1 indicate that annealing at higher temperatures accelerates crystallization as expected [13]. In addition, these results show that partial reaction ($h = 0.5$) also is responsible for increasing the degree of crystallization compared to samples made from dry ($h = 0$) solutions. In partially hydrolyzed films, the metal-oxygen-metal bonded oligomer acts as a molecular template for subsequent nucleation and crystallite growth. These results show that hydrolysis can be used to decrease the annealing temperature. In certain applications, such as the deposition of ferroelectric films on semiconductor substrates, lowering the processing temperature is beneficial to minimize reactions at the interface.

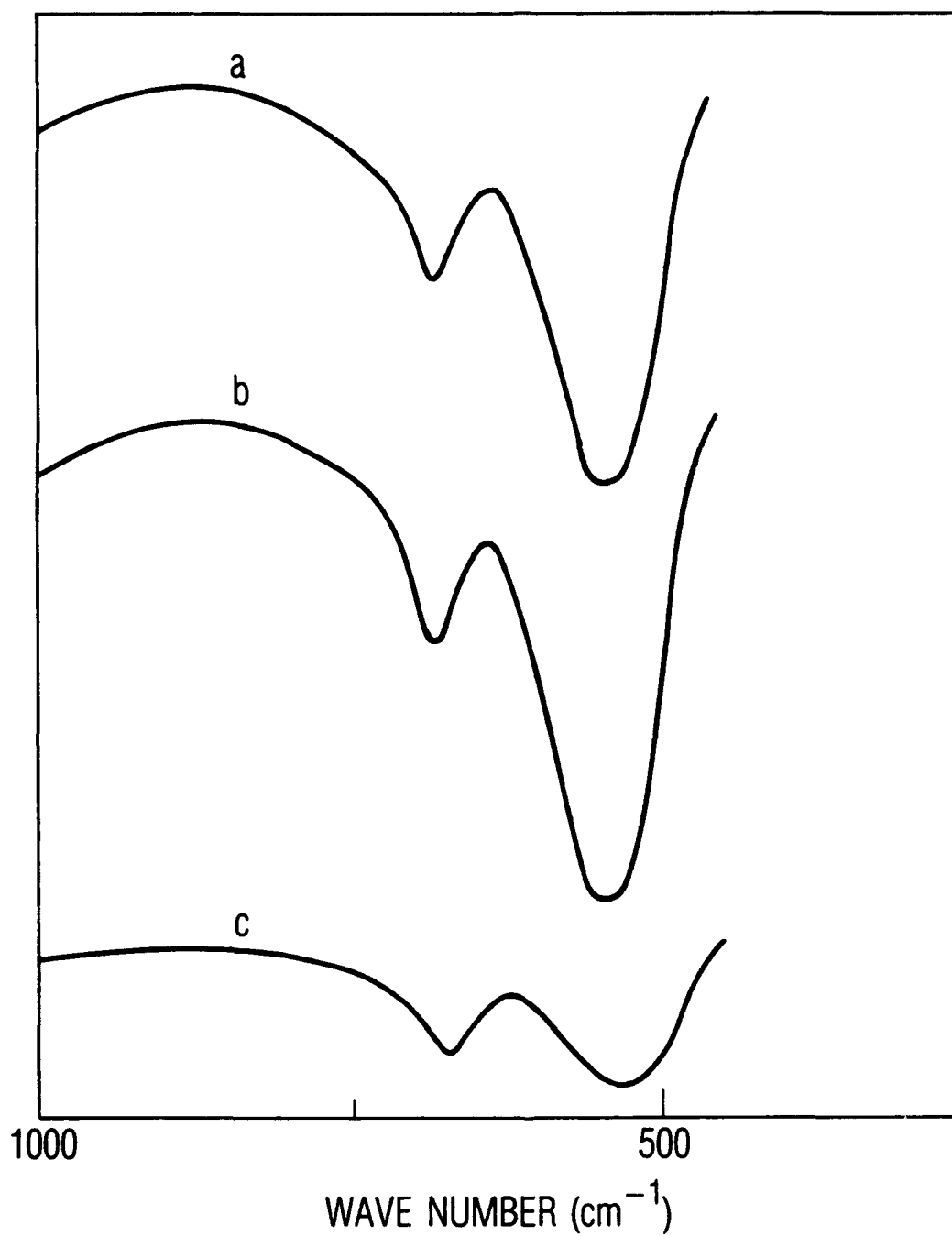
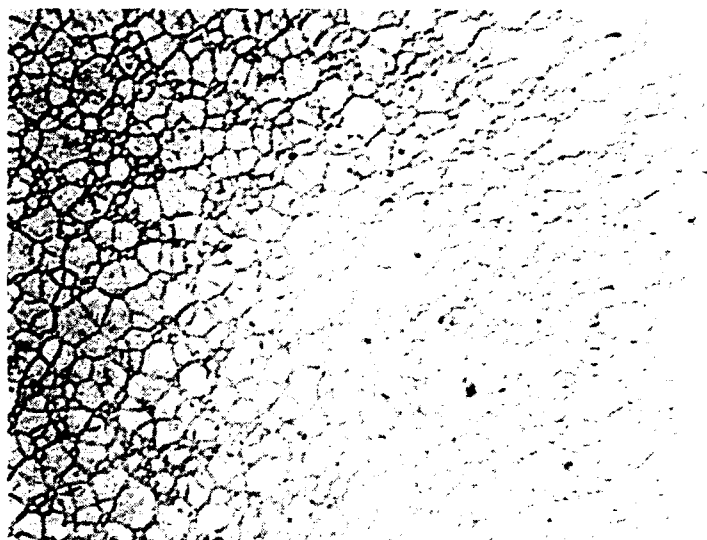


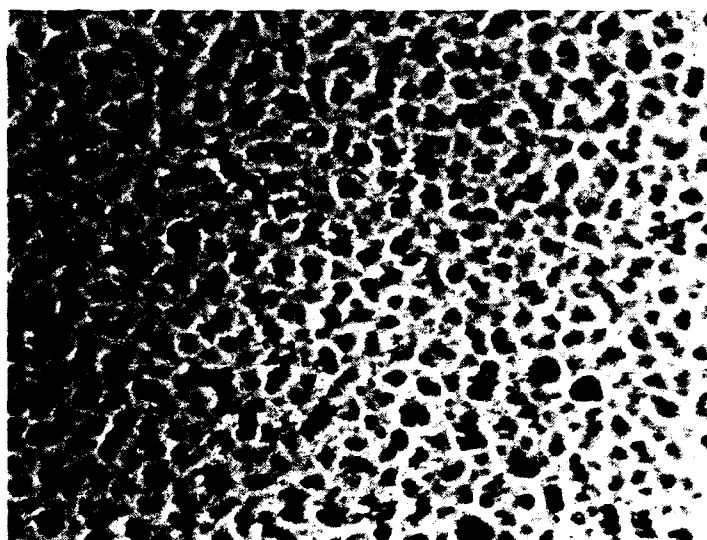
Figure 1. Spectral reflectance FTIR of 800 nm thick PZT films on platinum annealed at 525°C for 30 min with (a) $h = 0$, (b) $h = 0.5$, and (c) $h = 1.5$.



(a)



10 μm



(b)

Figure 2. Electron micrographs of PZT films annealed at 525°C with (a) $h = 0$ and (b) $h = 1.5$.

Table 1. Effect of Prehydrolysis and Annealing Conditions

Hydrolysis, h	Consolidation		Intensity of (110)
	Temperature, °C	Time, min	Diffraction peak, %
0	550	30	70
0	550	60	72
0.5	550	30	82
0	600	30	79
0.5	600	30	100
0.5	600	60	99

B. COMPOSITION

Bulk ceramic structure was obtained in 800 nm thick films prepared by MOSD in the PZT solid solution system. The phases present were determined in films where the zirconium-to-titanium ratio was varied from 60:40 to 0:100. After being annealed at 525°C for 2 h, the crystal structure of the films was characterized by x-ray diffraction. As smaller titanium ions were substituted for zirconium in PZT films, the lattice contracted, as shown from the data in Figure 3. A phase transition from rhombohedral to tetragonal occurred at about 0.52 PbZrO_3 in the film, as expected from the bulk ceramic data reported by Jaffe et al. [22]. This result indicates that the MOSD process can be used to prepare PZT with bulklike properties and that the phase diagram developed from bulk ceramic data can be used to guide the selection of composition and tailor the electronic properties of these thick films.

The micrographs in Figure 4 indicate that film quality depends on the composition of the film. Less cracking was observed in the 20:80 PZT composition (tetragonal structure) compared to the 60:40 composition (rhombohedral structure) films on fused silica substrates. During cooling through the Curie temperature, differences in thermal expansion between the film and the substrate can result in stress and cracking of the film. Lead titanate-rich PZT compositions expand during cooling through the Curie temperature as they change from a cubic to tetragonal structure [23]. Because the substrate contracts during cooling, the film is formed with compressive stress. Lead zirconate-rich films contract when they are cooled through their Curie temperatures [23], resulting in a film held in tension that is subject to cracking. The magnitude of these effects is dependent on the match of the thermal expansion coefficient of the film with that of the substrate. Lower stress and cracking is also correlated to lower diffuse light scattered from titanium-rich films, as shown in Figure 5. In addition to cracking, light is scattered in these films from grain boundaries and surface roughness. On fused silica substrates, high optical quality lead titanate films are easier to grow than compositions containing high lead zirconate concentrations.

We examined the effect of lead concentration in the films during processing. In films that were about 2% deficient in lead, nonuniform nucleation and segregation of a zirconium dioxide phase occurred. In films that were about 2% lead rich, lead oxide acted as a flux that avoided the formation of trace-contaminating oxide phases. Because the excess lead oxide tended to segregate on the edge of the substrate, it did not affect the quality of the films. The morphology of these films is shown in the optical micrographs in Figure 6. The lead-rich films have relatively few features, while the lead-poor films have large, coarse grains.

C. THERMAL TREATMENT

The perovskite crystal structure, easily obtained at high temperatures, is necessary for ferroelectricity in PZT films. However, in many applications, consolidation and crystallization must be achieved at the lowest possible temperatures. Low temperature processing minimizes microcracking by stress that results from differential thermal expansion of the substrate and

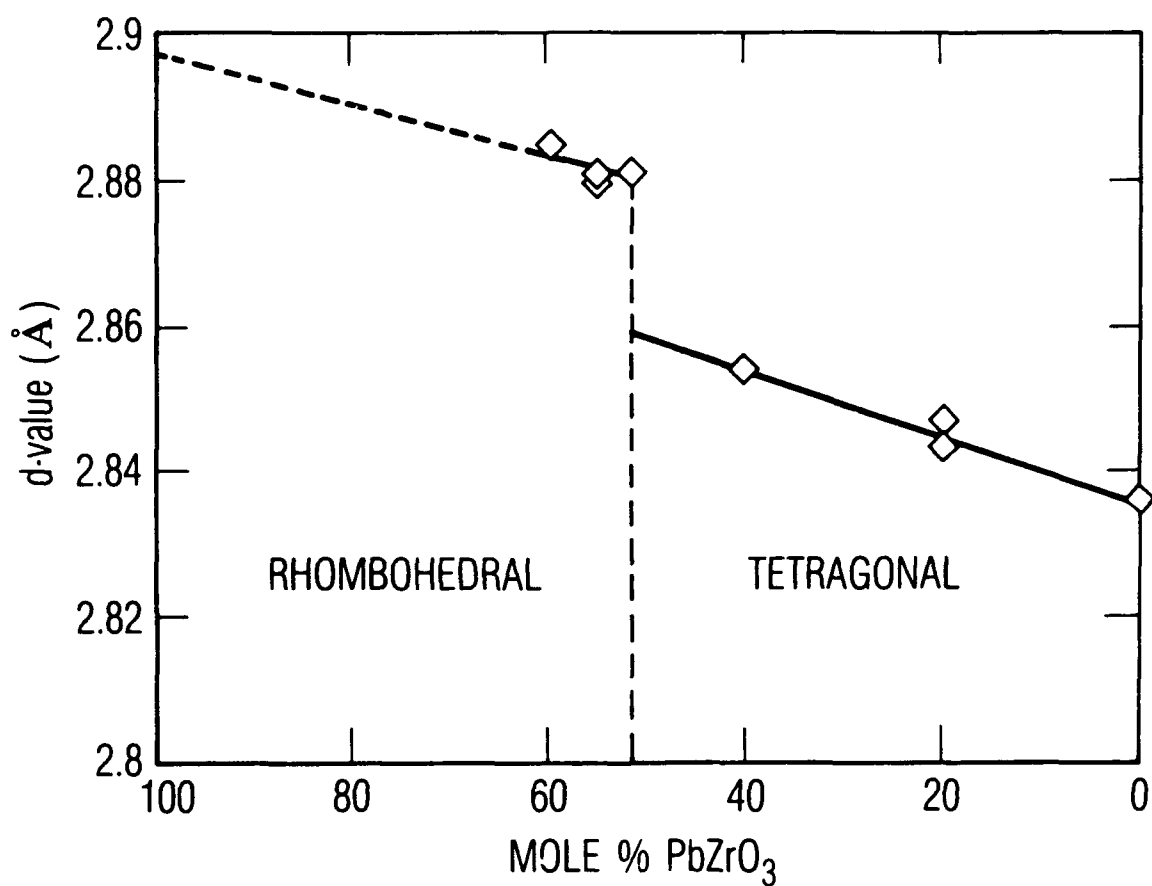
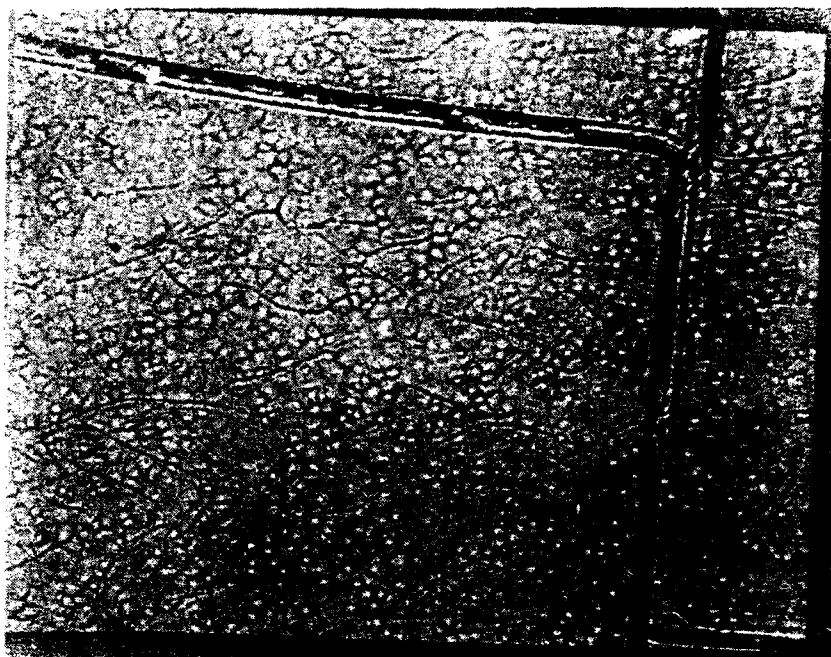
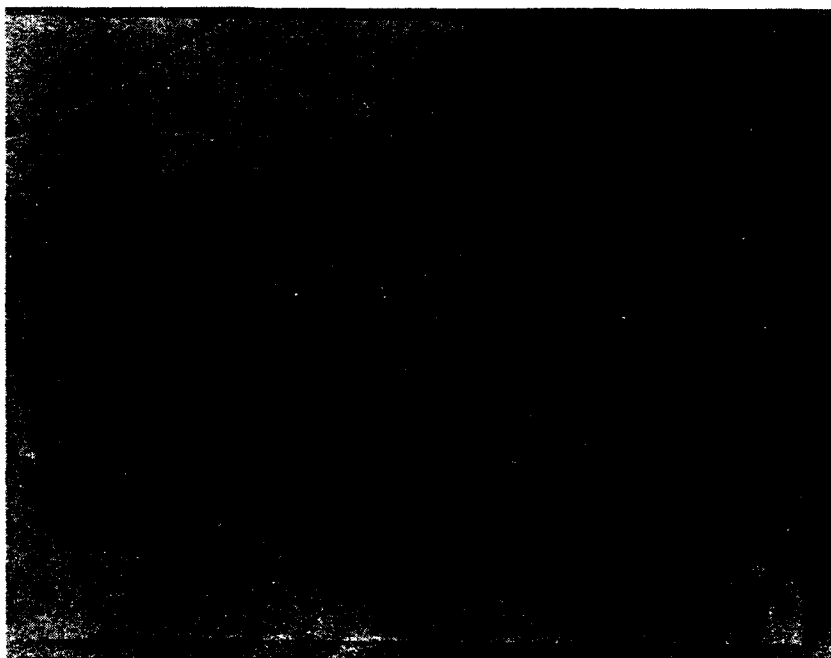


Figure 3. Lattice contraction due to titanium substitution for zirconium in PZT observed by x-ray diffraction in PZT films. Two regions were observed consistent with the ceramic: a high-zirconia rhombohedral phase and a high-titanate tetragonal phase.



(a)

20 μ m



(b)

Figure 4. Surface morphology of PZT films with (a) high zirconium concentration, 60:40, and (b) high titanium, 20:80. Note the presence of stress-induced microcracking and large cracks in (a), which is minimized in (b).

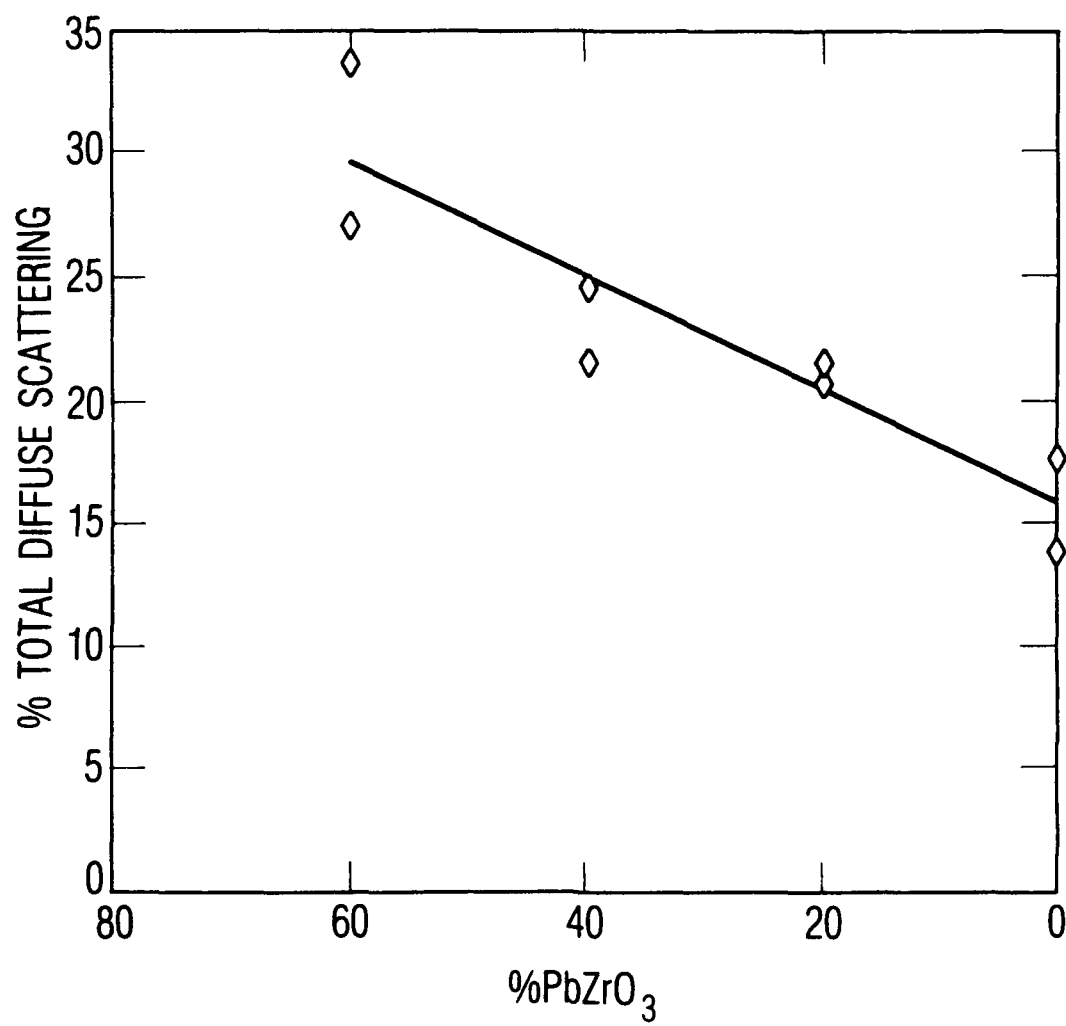
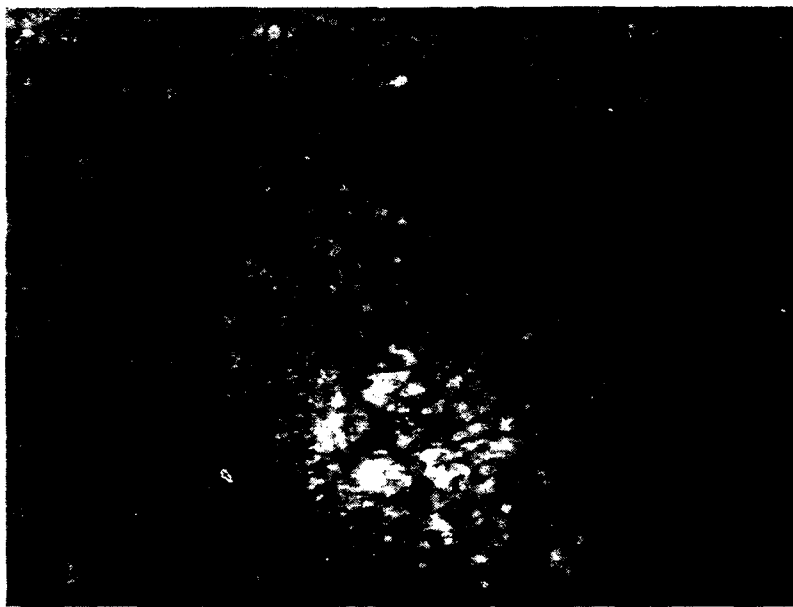


Figure 5. Light scattering from PZT films deposited on fused silica.



(a)

10 μm



(b)

Figure 6. Optical micrographs of PZT films processed with (a) excess lead oxide or (b) low lead oxide.

film. In addition, thermal diffusion and contamination of the film or substrate are reduced. Consolidation at low temperatures is particularly desirable to avoid reactions of the hot organic by-products with the substrate. In Figure 7, we show the effect of consolidation temperature on the crystallinity of films annealed at 550°C. In films consolidated at 500°C, the growth of the perovskite structure was reduced by the presence of a cubic pyrochlore-like phase related to $\text{Pb}_2\text{Ti}_2\text{O}_6$ [24]. The films consolidated at 300 and 400°C are perovskite [25], with a trace amount of the pyrochlore phase. The presence of the trace pyrochlore phase is further reduced at 600°C. These results and the time-temperature-transformation diagrams published by Chen et al. [14] indicate that PZT films can be consolidated (and annealed) at a wide range of temperatures. Selection of processing temperatures will depend on the reactivity and thermal expansion coefficients of the substrate and PZT film.

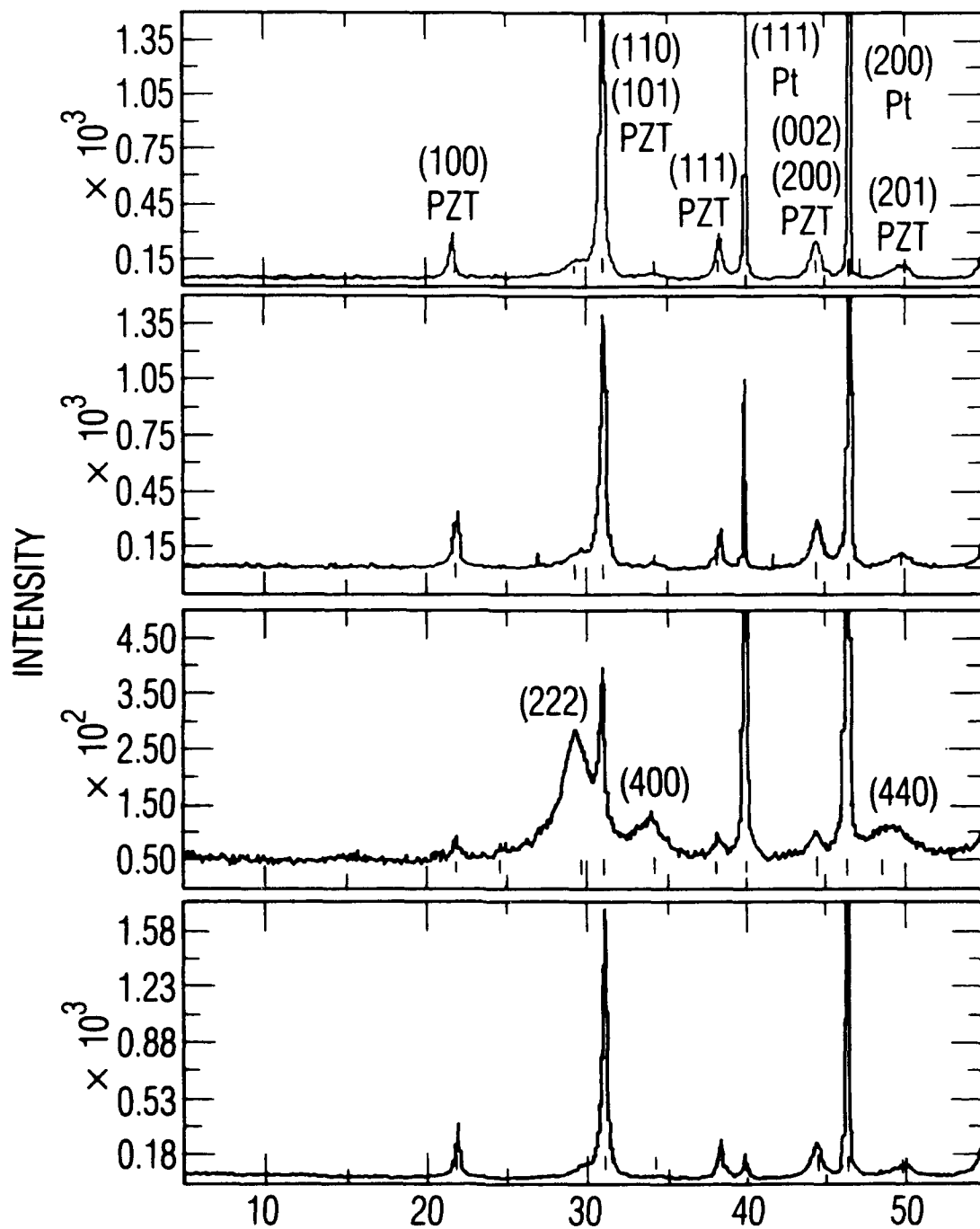


Figure 7. X-ray diffraction θ - 2θ scans of PZT films with a 52:48 composition deposited on platinum and consolidated at (from the top) 300, 400, 500, and 600°C.

V. SUMMARY

In summary, the MOSD technique can be used for making a wide range of PZT compositions with bulk structure and properties. Film morphology is affected by metal stoichiometry, hydrolysis and polymerization of the sol-gel solution, and thermal treatment. The PZT lattice parameter decreases with the amount of titanium in PZT, in agreement with ceramic data. A slight initial excess of lead in the coating solution improves film morphology. Unlike traditional powder ceramic techniques, MOSD permits the growth of small uniform grains. Films can be consolidated prior to crystallization at temperatures from 275 to 600°C, except for about 500°C, where the pyrochlore is stable. The ability to tailor these properties by the MOSD process will result in electro-optical films for new device applications.

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TECHNOLOGY OPERATIONS

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Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

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