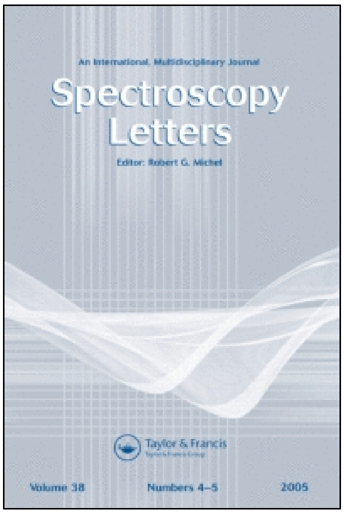

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Vibrational Spectral Characterization of a Lead Lanthanum Zirconate Titanate During Various Stages of Sol-Gel Processing

V. K. Seth[a]; W. A. Schulze[a]; R. A. Condrate Sr.[a]
[a] Center for Advanced Ceramic Technology NYS College of Ceramics Alfred University, Alfred, NY

To cite this Article Seth, V. K. , Schulze, W. A. and Condrate Sr., R. A.(1991) 'Vibrational Spectral Characterization of a Lead Lanthanum Zirconate Titanate During Various Stages of Sol-Gel Processing', Spectroscopy Letters, 24: 10, 1299 — 1315

To link to this Article: DOI: 10.1080/00387019108021763

URL: http://dx.doi.org/10.1080/00387019108021763

SPECTROSCOPY LETTERS, 24(10), 1299-1315 (1991)

VIBRATIONAL SPECTRAL CHARACTERIZATION OF A LEAD LANTHANUM ZIRCONATE TITANATE DURING VARIOUS STAGES OF SOL-GEL PROCESSING

KEY WORDS: Lead Lanthanum Zirconate Titanate, Sol-Gel, Infrared Spectra, Raman Spectra, Structure.

V.K. Seth, W.A. Schulze and R.A. Condrate, Sr.
Center for Advanced Ceramic Technology
NYS College of Ceramics
Alfred University, Alfred, NY 14802

ABSTRACT

Lead lanthanum Zirconate Titanate (PLZT 7/65/35) powders were prepared by a sol-gel process, using lead acetate, lanthanum acetate, zirconium n-propoxide and titanium n-propoxide as precursors along with 2-methoxyethanol as the solvent. Nitric acid was used to catalyze the sol-gel reaction. FTIR spectroscopy characterized the starting precursors, monitored the sol to gel transformations involving solutions with different molar ratios of water to alkoxide precursors, and tracked the crystallization behavior of the gels upon heat treatment. Raman spectroscopy was employed at room temperature to follow vibrational spectral changes for the samples that were cooled after various stages of heat treatment and crystallization of the

gels. The resulting spectral changes were analyzed in terms of the structural changes that occurred during the sol-gel process.

INTRODUCTION

Lanthanum doped lead zirconate titanate (PLZT) ceramics were the first electro-optic ceramics to be generated with extensive commercial applications.[1] The importance of the the role that chemical stoichiometry, porosity, grain sizes and impurities in the fabricated ceramic material plays in terms of its final physical and chemical properties must be underscored. Realizing that the nature of the starting materials plays a vital role in influencing the fabrication parameters to form a theoretically dense, high purity, fine grained ceramic oxide structures, metal alkoxides have been utilized in the preparation of PLZT materials.[2] Their reaction processes involve sol-gel technology which yields high-purity powders with submicron particle sizes. Their heat treatment stages usually utilize temperatures which are much lower than those required during conventional mixed-oxides processing. This technique enables the fabrication of not only submicron powders but also thin films and fibers. Various electroceramic powders have been prepared by such processing techniques, resulting in ceramics with enhanced properties.[3]

Infrared and Raman spectroscopy can be used as complimentary techniques to investigate the structural arrangements in materials containing perovskite oxides. The Raman spectra of perovskite ferroelectrics are rich in details concerning the symmetry types and the band characteristics of their scattering phonons. However, certain first order bands can be absent in the Raman spectra of crystals which are centrosymmetric. This possibility occurs for optical phonon modes of cubic perovskite ferroelectrics. Lurio and Burns[4] reported Raman scattering results for PLZT materials which do not have this problem at the investigated temperatures. The Raman spectrum of antiferroelectric $PbZrO_3$ which relates to PLZT materials has also been investigated in detail.[5] Corresponding infrared spectral data have also been investigated for PLZT.[4]

For an ordered crystal, the vibrational bands observed in the IR and Raman spectra that correspond to $k = 0$ phonon modes are sharp. These bands are broadened or replaced by a broad continua when the crystal structure is disordered due to the breakdown of the $k = 0$ selection rules.[6,7] The lead zirconate titanate family possesses a disordered structure.[8] Each composition, irrespective of the relative amounts of the two B-site ions, is completely disordered. Upon substitution of lead by lanthanum, the crystal structural arrangement is not expected to change dramatically.

This current study has focussed on the infrared and Raman spectral investigation of the evolution of PLZT powders from precursor solutions containing organometallic species by means of a sol-gel process. Such spectral investigations can analyze the structural changes that occur in the polymers which form in the sol and the gel, and their behavior during the heat treatment. With such detailed characterization of the process, an understanding of the development of the desirable phase is made possible which may be used to optimize the fabrication technique.

EXPERIMENTAL PROCEDURES

PLZT 7/65/35 was prepared by using a sol-gel technique similar to those utilized by Gurkovich et al.[9] and Budd et al.[10] except with a few modifications. The starting materials included lead acetate trihydrate, lanthanum acetate hydrate, zirconium n-propoxide and titanium n-propoxide along with 2-methoxyethanol as the solvent. The hydrolysis reaction was catalyzed using 0.1 M HNO_3 acid. Fig. 1 illustrates the flow chart that summarizes the procedure for the preparation of the powder products.[11] S is the molar ratio

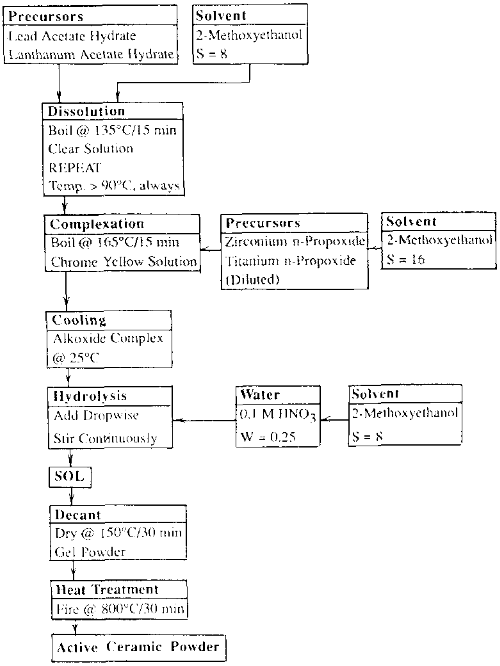

Fig. 1. Flow chart for the sol-gel preparation of PLZT 7/65/35 powder.

of the solvent (2-methoxyethanol) to the alkoxide complex, while W is the molar ratio of the hydrolysis water (actually, water from added nitric acid) to the alkoxide complex. Fig. 2 illustrates the experimental set-up that was used to prepare the alkoxide complexes.

FTIR spectra were measured on a Nicolet 60SXR FTIR spectrometer with an air-purging device using either a KBr window technique for liquids and semi-liquids or the KBr pellet technique for powders. IR spectra of the original starting materials and their transformation to alkoxide complexes were monitored. Sol to gel transformations were studied with respect to the time elapsed after the hydrolysis catalyst was added, using FTIR spectroscopy. Sol-gel preparations involving various W-values were investigated. Thermogravimetric analysis was conducted on dried gels in order to observe

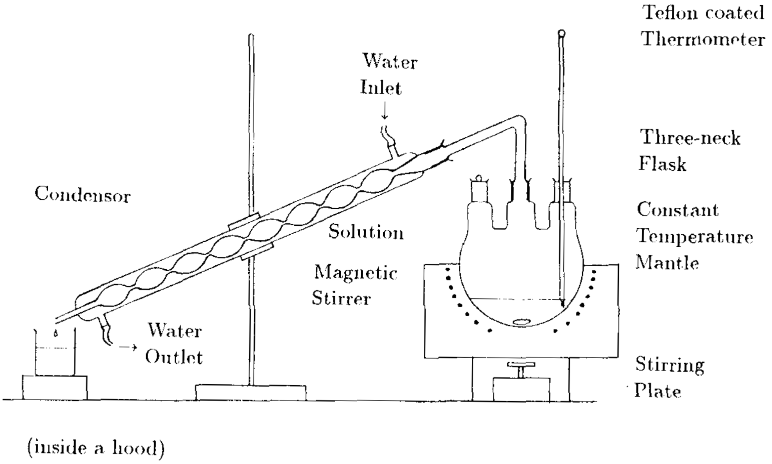

Fig. 2. Experimental set-up for preparation of the alkoxide complex solution.

the burnout behavior of the organic fractions. Gel crystallization behavior was studied using both FTIR spectroscopy and X-ray diffraction analysis.

Room-temperature Raman spectroscopy was also utilized as an additional tool to investigate the crystallization behavior of the gel. An Instrument SA U1000 double grating spectrometer with a CR argon ion laser (514.5 nm) was employed, using 90° optics. The capillary technique was applied for these Raman spectral measurements.

RESULTS AND DISCUSSION

The sol-gel fabrication process utilized here can be segmented into three individual transformations (Precursors → Sol → Gel → Crystals). FTIR spectroscopy was utilized to study all of these transformations while Raman spectroscopy was used only for the gel to crystal transformation.

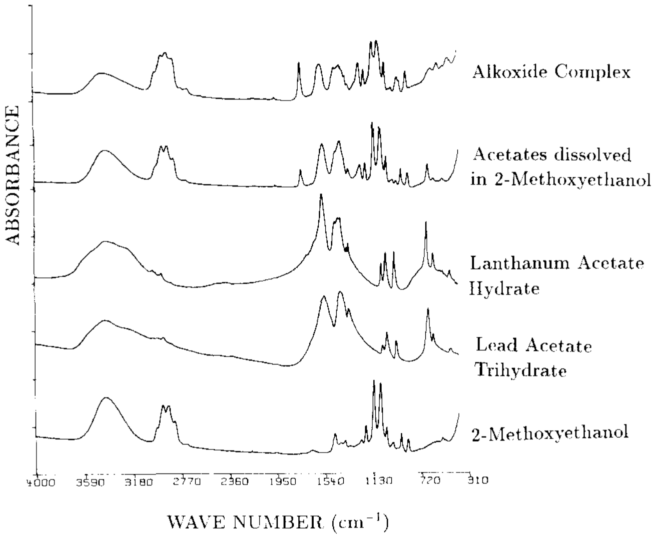

Fig. 3. Infrared spectra measured during formation of the alkoxide complex solution.

A. Formation of Solutions from Precursors

Fig. 3 illustrates the IR spectra of the metal acetates utilized in the process, and the alkoxide complexes that were formed upon dissolution of the acetates and alkoxides into solution. Characteristic dominant bands occurred for 2-methoxyethanol at ca. 1050, 2900 and 3410 cm^{-1}. Useful IR bands occurred for the acetates of both lead and lanthanum at ca. 1410 and 1550 cm^{-1}. Acetate esters and/or acetic acid possibly may be formed upon dissolution of such acetates in 2-methoxyethanol under the conditions of this preparation. This possibility was suggested by the presence of a band at ca. 1730 cm^{-1}. No new band appeared in the discussed region for the acetates upon the additional dissolution of lanthanum acetate into the solution containing lead acetate. This result suggests that lanthanum acetate formed bidentate complexes in the solution similar to lead acetate.[12] Upon complete addition of the zirconium and titanium alkoxides to the solutions containing lead and lanthanum acetate (thereby forming alkoxide complex solutions with the appropriate cation molar ratios for eventually generating the desired perovskite oxide), the IR bands related to bidentate complexes did not disappear even with aging. This spectral result seems to indicate that bimetallic complexes mainly were formed in solutions which contained metal-oxygen-metal linkages involving lead or lanthanum ions with either zirconium or titanium ions rather than trimetallic complexes which contained metal-oxygen-metal-oxygen-metal linkages involving lead or lanthanum ions as the central metal ions. Significant retention of IR bands associated with bidentate metal acetate complexes in the solutions and later in heat-treated gels also strongly argues against the possibility of dominant amounts of a polymeric metal alkoxide species[13] over the bimetallic complex species for the solutions formed under our conditions of preparation. This interpretation is similar and consistent with the interpretation of spectral changes during the sol-gel preparation of PZT materials.[12]

B. Transformation of Solutions to Sols to Gels

The hydrolysis step in the sol-gel process was very important because it initiated the gelation process. Furthermore, the amount of water that was used in this step was critical because its reaction provided the sites that were necessary for linkage formation during the polymerization process. While water was consumed during hydrolysis, it was regenerated during the polycondensation process. In the presence of excess water, the condensation reaction was slowed down in accordance with Le Chatelier's principle, and hence, affected the cross-linking of the polymers. The resulting polymeric structure influences the microstructure of the final ceramic product.

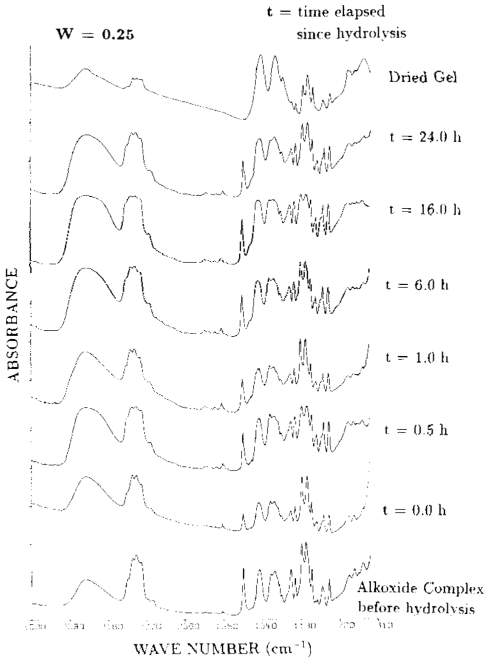

Fig. 4. Infrared Spectra measured during gelling process for the solution with W = 0.25.

The evolution of the dried gel products from the hydrolysis and polycondensation of the alkoxide complexes for various values of W was investigated by using FTIR spectroscopy. The utilized values of W were 0.25, 0.5, 1.0, 2.5 and 4.0. Since the trends in the spectral changes were very similar for various values of W (although the absolute values of the relative intensities differed for bands associated with various species that were present in the materials) during various stages of the gelation process, The FTIR spectral series is illustrated in Fig. 4 for the gelation process involving W equal to 0.25. The IR band observed at 1730 cm^{-1} that was related to the presence of esters eventually disappeared upon gel formation. However, the band as-

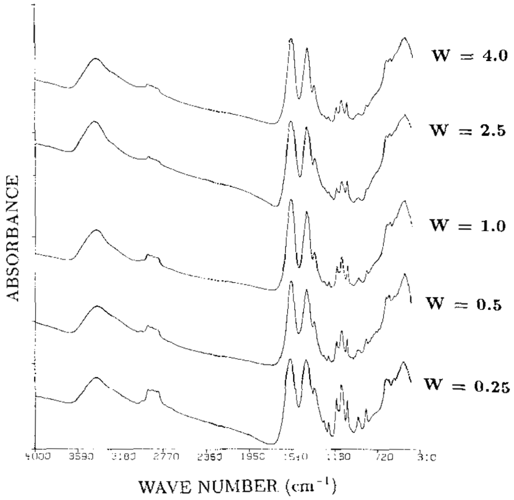

Fig. 5. Infrared spectra of dried gels prepared with various W-values.

sociated with bidentate complexes persisted even for the dried gels. Similar trends were noted earlier for PZT materials.[12] The infrared bands associated with Zr-O and Ti-O stretching modes occurred in the 460 - 600 cm^{-1} range. For all values of W, the intensities of the bands for these stretching modes increased as the treatment time progressed, and reached a maxima for the dried gel. Analyzing all investigated series of IR spectra, one notes the growth in the intensity of the O-H stretching mode at 3410 cm^{-1} upon the addition of hydrolysis water, and its eventual decrease to a minimum in the dried gel.

Fig. 5 illustrates the IR spectra for the dried gels prepared with various values of W. The relative band intensities in the spectra for all values of W are similar except for the bands especially in the vicinity of 1050 cm^{-1} (namely, 1125, 1066 and 1018 cm^{-1}). These bands correspond to dominant bands for 2-methoxyethanol, which is the solvent that was used in the process (See Fig. 3). The observed relative intensity patterns for these IR bands associated with 2-methoxyethanol may be due to differences with respect to W in its adsorption on the resulting surfaces of the polymeric structures which constitute the matrices of the dried gels. The maximum relative intensities of these bands occurred for samples prepared with W = 0.25, suggesting that maximum surface area for the polymeric structures in samples results with this W-value. Hence, small linear chain-like polymers (rather than large spherical polymeric structures) are present in the sols with low water content and low pH, resulting in higher surface area on which the solvent is adsorbed. Using spectral analyses of such vibrational bands for various sols may help in the selection of proper sol preparation conditions that are suitable for commercially-useful film formation.

C. Gel to Crystal Transformations

Thermogravimetric analysis (TGA) was applied to the dried gel that was prepared with W = 0.25. Data indicated that the organic burnout was completed by 550°C. XRD analysis also indicated that the development of the same crystalline pyrochlore phase had occurred in all dried gels (W varying from 0.25 to 4.0) after a heat treatment at 550°C for 1 hour (See Fig. 6). Garvie[14] observed interesting behavior with active ZrO_2 powder, for which the high-temperature tetragonal phase was synthesized as a stable phase at room temperature instead of the normally-expected monoclinic phase. Upon heat treatment of the material, the monoclinic phase was formed as the crystallites grew. He pointed out that a critical crystallite size existed below which the high-temperature phase could exist as a metastable phase at room temperature. Later, Garvie[15] proposed that the stabilization of the high-temperature phase by crystallite size control may be a general phenomenon resulting from a structural phase transformation associated with an

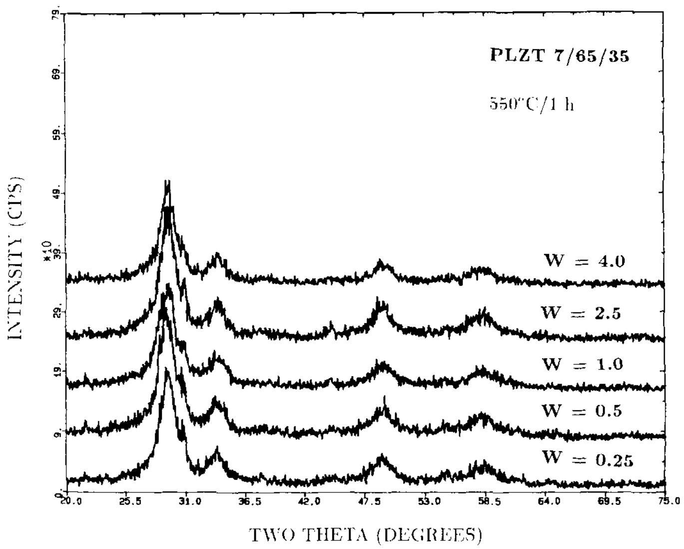

Fig. 6. X-ray diffraction patterns of dried gels prepared with various values of W that were heat-treated at 550° for one hour.

endothermic heat effect during heating. Indeed, barium titanate has been observed as the cubic phase (instead of the expected tetragonal phase) at room temperature for crystals possessing particle sizes of 10 nm.[16] As the amorphous gel in the current investigation transits through this particle size range during crystal growth from the gel, this mechanism should be operative, resulting in the formation of a metastable pyrochlore-type phase for PLZT 7/65/35.

Analysis of the x-ray diffraction patterns in Fig. 7 indicates the crystallization behavior of the dried gel upon treatment at 500°C and higher temperatures. Heat treatment time was one hour at each investigated temperature. The amorphous dried gel first formed a metastable intermediate pyrochlore-type phase which then transformed to a phase-pure pervoskite

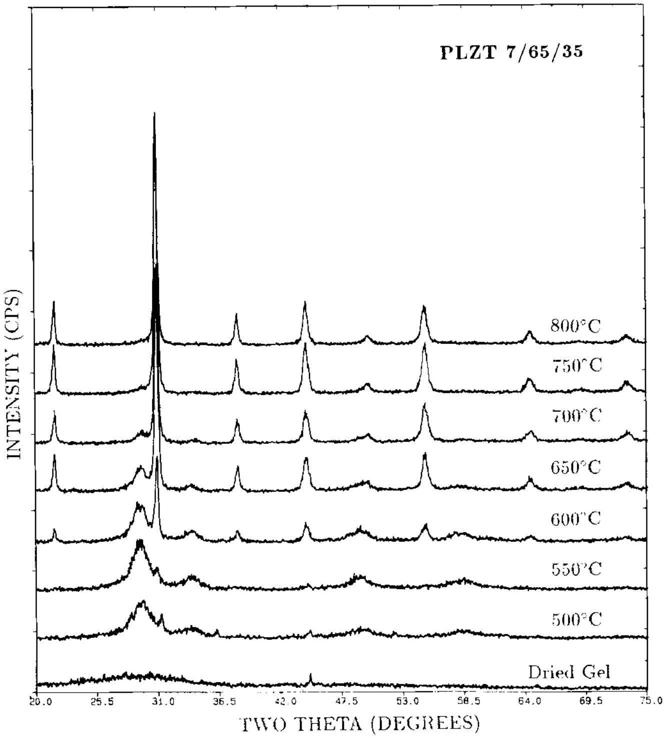

Fig. 7. X-ray diffraction patterns of gel powders heat-treated at various temperatures for one hour.

PLZT (7/65/35) material at ca. 750°C. Fig. 8 illustrates the IR spectra of the powders that were heat treated at various temperatures for one hour. All traces of the bidentate complexes were eliminated after heat treatment at 600°C. The intensities and the sharpness of the IR bands in the 460 - 600 cm^{-1} range which correspond to Zr-O and Ti-O stretching modes increased with an increase in heat treatment temperature. This spectral change traces the evolution of the octahedral cages of oxygens surrounding Zr or Ti ions

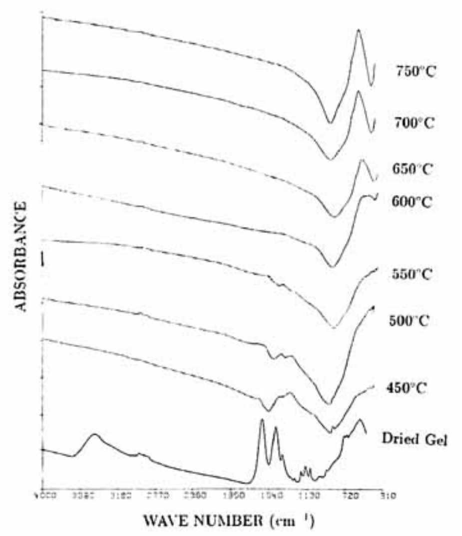

Fig. 8. Infrared spectra of gel powders heat-treated at various temperatures for one hour.

in the perovskite structure. Also, one may note that a psuedo reststrahlen or reflectance effect was observed at higher temperatures from the bidentate complexes before their complete elimination at ca. 600°C.

Fig. 9 illustrates the Raman spectra of the gel powder at room temperature after heating the sample at various temperatures during its crystallization to a phase-pure perovskite PLZT 7/65/35 powder. The spectra possessed the dominant Raman band corresponding to the polar perovskite phase at 470 cm^{-1} when this phase appeared in the sample (See Fig. 7). Increase in amount of this phase in the sample upon increase of the processing temperature is reflected in the sharpening and the increase in the intensity for the Raman band at 470 cm^{-1}. After heat treating the samples at 650°C or higher temperatures for the investigated treatment periods, the predomi-

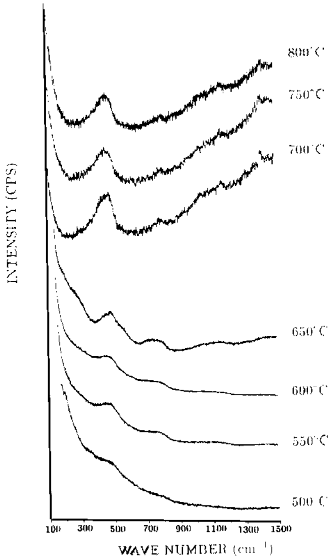

Fig. 9. Raman spectra of gel powders heat-treated at various temperatures for one hour.

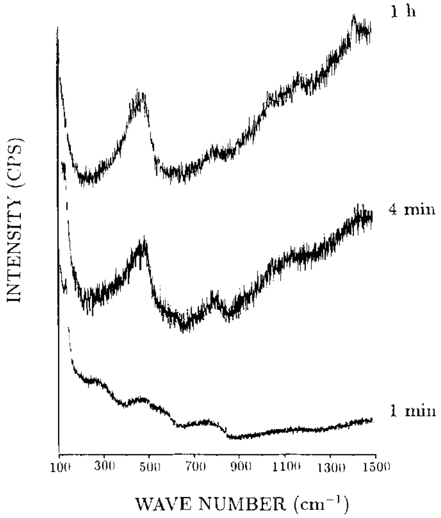

Fig. 10. Raman spectra of gel powders heat-treated at 700° for various times.

nant phase that was present in the powder was the perovskite phase whose band features strongly dominated the resulting Raman spectra.

Powders with varying amounts of pyrochlore content were prepared by rapid thermal processing of the gel powders at 700°C for various treatment times in order to obtain stronger Raman spectral features for the pyrochlore component in the solid material. Analysis of the x-ray diffraction patterns for powders that were fired for one minute and four minutes indicated that they contained 36 % and 83 % perovskite phase, respectively. As would be expected, the band features of the perovskite phase completely dominated the room-temperature Raman spectra of the gel powders fired for four minutes and one hour(See Fig. 10). However, the room-temperature Raman spectra of the powdered gel that was fired for one minute (See Fig. 10) contained band features of comparable intensity to those of the perovskite phase that can be assigned to another phase. The band at ca. 290 cm^{-1} corresponded to the dominant Raman band noted in approximately this region for zirconate pyrochlore phases.[17,18] Other spectral details related to this latter phase. One may further note that the bands corresponding to the perovskite structure steadily developed in sharpness and intensity with an increase in firing time.

CONCLUSIONS

This study monitored the evolution of the precursor solutions to the final ceramic oxide powder of PLZT 7/65/35 during various stages of the investigated sol-gel processing by utilizing IR and Raman spectroscopy. The resulting structural changes that occurred during the investigated transformations (precursor → sol → gel → crystals) could be successfully sequenced. Characterization data clearly indicated the formation of an intermediate pyrochlore phase during firing of gels. The analysis of the complete results suggested that such in-depth vibrational spectral analyses can be utilized to optimize the sol preparation, and to determine their suitability for film formation.

REFERENCES

1. Haertling G.H. and Land C.E., J. Amer. Ceram. Soc., 54, 1 (1971).
2. Brown L.M. and Mazdiyasni K.S., J. Amer. Ceram. Soc., 55, 541 (1972).
3. Ozaki Y., Ferroelec., 49, 285 (1983).
4. Lurio A. and Burns G., J. Appl. Phys., 45, 1986 (1974).
5. Pasto A.E. and Condrate R.A., Sr., J. Amer. Ceram. Soc., 56, 436 (1973).
6. Keramidas V.G. and White W.B., J. Phys. and Chem. Solids, 34, 1873 (1973).
7. Whalley E. and Bertie J.E., J. Chem. Phys., 46, 1264 (1967).
8. Galasso F.S., Structure, Properties and Preparation of Perovskite Type Compounds, Pergamon Press, London, 1969.
9. Gurkovich S.R. and Blum J.B., Ultrastructure Processing of Ceramics and Composites, pp. 152-160, Edited by L.L. Hench and D.R. Ulrich, Wiley-Interscience, New York, 1984.
10. Budd K.D., Dey S.K. and Payne D.A., Proc. Brit. Ceram. Soc., 36, 107 (1985).
11. Vinay Seth, Ph.D. Thesis, Alfred University (1990).

12. Li S., Condrate, R.A., Sr. and Spriggs R.M., J. Can. Ceram. Soc., 57, 61 (1988).

13. Dekleva T.W., Hayes J.M., Cross L.E. and Geoffroy G.L., J. Amer. Ceram. Soc., 71, C-280 (1988).

14. Garvie R.C., J. Phys. Chem., 69, 1238 (1965).

15. Garvie R.C., J. Phys. Chem., 82, 218 (1978).

16. Takada T. and Kawai N., J. Phys. Soc.(Japan), 17, Supplement B-1, 691 (1962).

17. Michel D., Jorba M. P. y and Collongues R., Mater. Res. Bull., 9, 1457 (1974).

18. Vandenborre M.T. and Husson E., J. Solid State Chem. 50, 362 (1983).

Date Received: 07/03/91
Date Accepted: 08/06/91