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FTIR and Raman spectral study of the preparation of lead zirconate ($PbZrO_3$) by a sol–gel process in a non-flowing air atmosphere

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Lead zirconate (PZ) materials were prepared by a sol–gel process in a non-flowing air atmosphere with no continuous agitation using lead acetate and zirconium propoxide in methoxyethanol as the precursor materials. Fourier transform infrared and Raman spectroscopy were used to characterize the structural changes that occurred during various stages of this preparation. Crystalline phase formation differences were noted during this sol–gel preparation for PZ in comparison to those occurring during the related preparation for lead titanate (PT). Metallic lead and lead oxide (PbO) were formed during the heating steps of this process in an air atmosphere for PZ. *In situ* Raman spectra were also measured at higher temperatures for the resulting sol–gel prepared $PbZrO_3$ material in order to investigate its phase-transition and soft-mode behaviour.

1. Introduction

Materials in the lead zirconotitanate (PZT) system possess useful industrial applications because of their electro-optical and piezoelectric properties. Sol–gel techniques provide convenient methods to prepare films of these materials. The final properties of the resulting materials are dependent upon the structural changes that occur during their preparation. Fourier transform infrared (FTIR) and Raman spectroscopy provide convenient techniques to investigate such structural changes during their preparation. Shu Li *et al.* [1] have investigated with these spectral techniques such changes that occur during the sol–gel preparation of lead titanate. The current investigation extends such spectral/structural studies to the sol–gel preparation of lead zirconate (PZ) materials. Differences in the formation of various phases during various preparation steps will be noted for PZ materials in comparison to those for PT materials. The phase-transition and soft-mode behaviour of the resulting sol–gel prepared PZ materials will also be investigated using *in situ* Raman spectroscopy at high temperatures.

2. Experimental procedures

Lead zirconate (PZ) materials were prepared essentially using the procedures described earlier by Shu Li *et al.* for the preparation of PT materials [1, 2]. The precursor materials used in this study were lead acetate ($Pb(OAc)_2 \cdot 3H_2O$), zirconium propoxide ($Zr(prop)_4$) and methoxyethanol. The process involved dissolving the metal-containing compounds in the solvent, hydrolysing and polycondensing the resulting solution into a gel, and finally heat-treating the gel to form the perovskite PZ product. Details of the PZ preparation concerning parameters such as solute concentrations, applied hydrolysis water contents, heating temperatures and schedules, etc., may be found elsewhere [2].

FTIR spectra were measured for both liquid and powder samples at various stages of the sol–gel process using a Nicolet 60SXR FTIR spectrometer with an air purging device. Liquid samples were placed for measurement between KBr windows. Powdered samples were mixed and pressed with KBr powder to form pellets which could be spectrally investigated using the KBr pellet method. The materials were monitored at all stages of this process using FTIR spectra.

Raman spectra were measured with an Instruments SA U1000 double grating spectrometer using 90° optics and a CL Innova 90 argon-ion laser. The green laser line (514.5 nm) was used in this study for all Raman measurements. Because of fluorescence problems, Raman spectra are only illustrated for the samples that were heat-treated to burn off all of the organic species. *In situ* Raman spectral measurements were made at high temperatures using a specially designed water-cooled high-temperature cell. Details of this cell are presented elsewhere [2].

Powder X-ray diffraction patterns were measured with an automated Norelco powder X-ray diffractometer using Cu$K\alpha$ radiation with a single crystal graphite monochrometer. Capacitances which were used to determine dielectric constants were measured with a Hewlett Packard LF Impedance Analyser Model 4192A.

3. Results and discussion

The structural interpretation of the vibrational spectra during various stages of the applied sol–gel and crystallization processes for the PZ materials investigated

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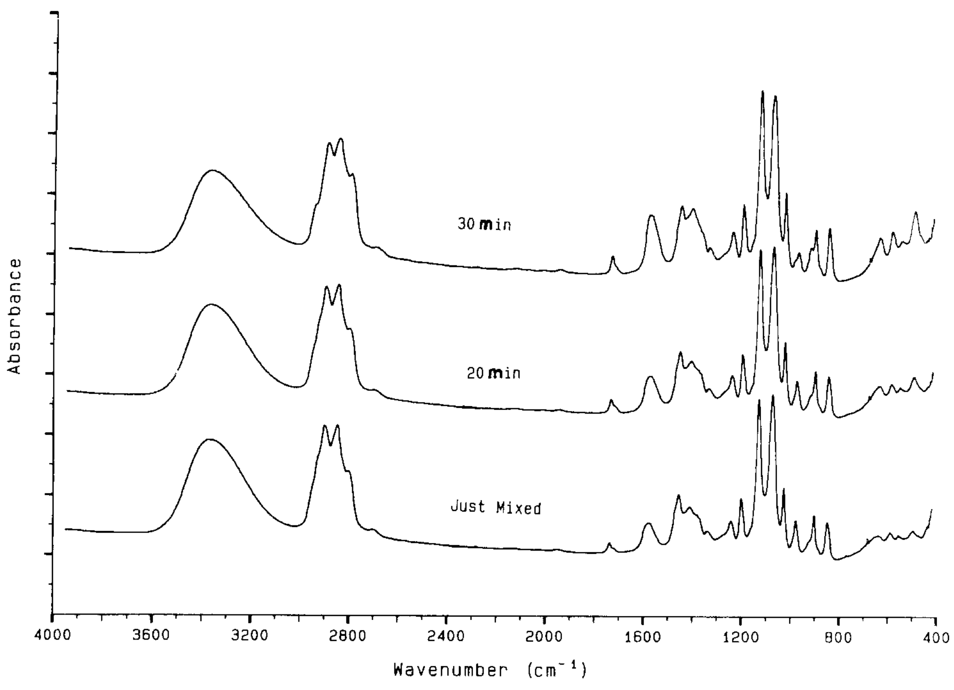


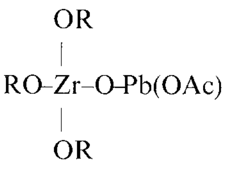
Figure 1 FTIR spectra of solutions containing lead acetate and zirconium propoxide.

will be discussed in this section. First, the vibrational spectra that were measured at room temperature for these samples after various stages of treatment will be discussed in terms of the structural units that were present in the liquid solutions, gels and crystalline phases. Finally, *in situ* Raman spectra obtained for the resulting PZ material at various high temperatures will be discussed in terms of the spectral changes and phase-transformation that occur through the Curie point.

3.1. FTIR spectra of the solutions before hydrolysis

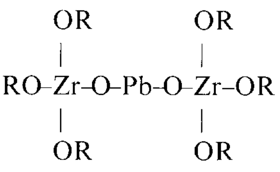
As noted in the earlier sol–gel study for PT materials, several significant changes were observed in the FTIR spectra when lead acetate was dissolved and heated in methoxyethanol [1]. The H–O–H bending mode at 1654 cm^{-1} was still observed when the acetate was just dissolved into the solvent. It did not disappear until the solution was distilled for 20 min. Also, the asymmetric COO stretching mode shifted in contrast to that for crystalline lead acetate to a higher wavenumber (~ 1558 cm^{-1}), indicating that the lead and acetate ions in solution involved only bidentate complex bonding [1]. The bridging type of complex formation between lead and acetate ions that occurs in the crystalline phase was not present in the solution on the basis of the changes occurring in the vibrational spectra upon solution formation [1]. Also, a weak infrared band at ~ 1740 cm^{-1} indicated the presence of a very small amount of ester and/or free acid after distilling.

Fig. 1 illustrates the FTIR spectra of the methoxyethanol solution containing lead acetate after $Zr(prop)_4$ addition. Ester formation occurred in the solution as indicated by the growth of the band at ~ 1740 cm^{-1}. The intensity of this band was stronger for this solution after $Zr(prop)_4$ addition than before the addition. The wavenumber of the asymmetric COO stretching mode shifted due to addition of the alkoxide (~ 1576 cm^{-1}). This shifting may be an indication of the formation of a bimetallic species (I). The strong intensity of this band is an indication that a trimetallic species (II) in not a dominant species in the solution.



$$\begin{array}{ccc} & \mathrm{OR} & \\ & | & \\ \mathrm{RO{-}} & \mathrm{Zr} & \mathrm{{-}O{-}Pb(OAc)} \\ & | & \\ & \mathrm{OR} & \end{array}$$

(I)



$$\begin{array}{ccccc} & \mathrm{OR} & & \mathrm{OR} & \\ & | & & | & \\ \mathrm{RO{-}} & \mathrm{Zr} & \mathrm{{-}O{-}Pb{-}O{-}} & \mathrm{Zr} & \mathrm{{-}OR} \\ & | & & | & \\ & \mathrm{OR} & & \mathrm{OR} & \end{array}$$

(II)

If this latter species were completely formed, this band would disappear because acetate ester would be the dominant acetate-containing species. In contrast to the study with $Ti(prop)_4$, the intensity of the band at ~ 1740 cm^{-1} relative to that of the band at ~ 1576 cm^{-1} did not dramatically change after mixing as one increased the ageing time, indicating that the kinetics for the formation of species I during prehydrolysis is probably faster for the zirconium alkoxide. As solution was distilled (losing alcohol and some ester), the intensity of the infrared bands for the lead acetate species increased with respect to those of the solvent. Distinct Zr–O bands formed in the low wavenumber region upon alkoxide addition, and they remained essentially unchanged during the distillation, also indicating the almost instantaneous and complete formation of species I upon the addition.

3.2. FTIR spectra of the solutions after hydrolysis

Fig. 2 illustrates the FTIR spectra for samples during hydrolysis and its related ageing process. Both ester and alcohol evaporated during the polycondensation process. The intensities of the alcohol bands gradually decreased during this process, indicating alcohol loss. However, some solvent remained in the gel even during the final spectral measurement during this stage. The ester C=O stretching mode did not

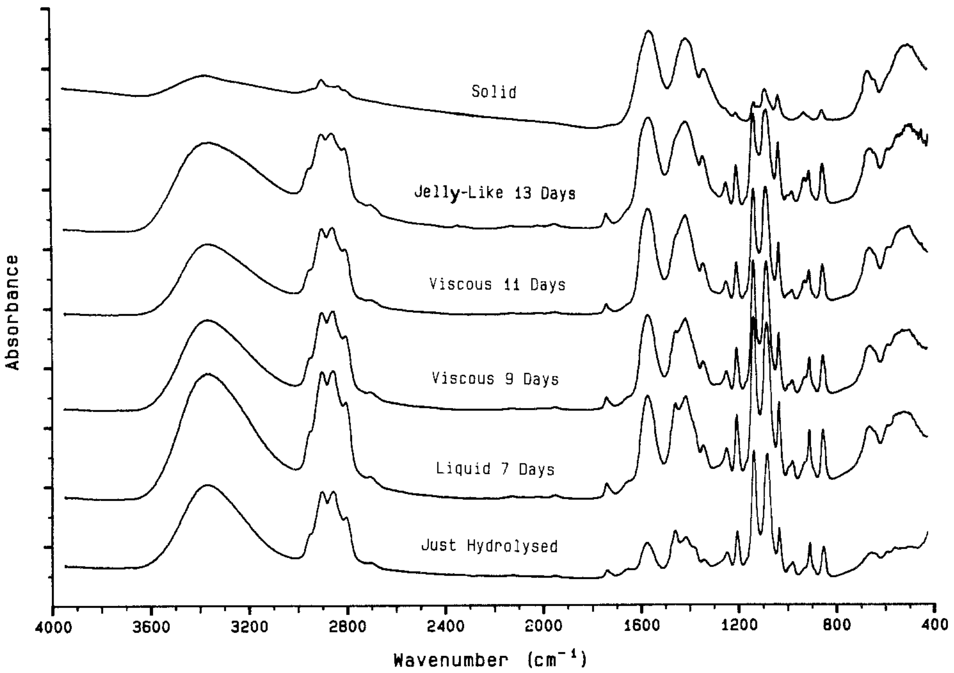


Figure 2 FTIR spectra of the gelation of $PbZrO_3$ materials.

disappear until the gel solidified, at which stage the ester was no longer present in the gel. The loss of water during hydrolysis and polycondensation could be followed on the basis of the intensity of the H–O–H bending mode. Bands associated with lead acetate complexes remained during the gelling process, indicating that these structural units were retained during the gelling process. Apparently, no new types of linkage involving Pb–O bonds were formed during polycondensation, although Zr–O–Zr linkages were formed.

3.3. FTIR and Raman spectra of the samples after heat treatment

Fig. 3 illustrates the FTIR spectra for the PZ materials after various stages of heat treatment in an air atmosphere. The bands that are associated with alcohol including those for the O–H and C–H stretching modes essentially disappeared upon heat treatment. The FTIR spectral analysis indicated that acetate species disappeared with heat treatment at temperatures varying from 300 to 400° C. Zr–O modes that are typical for crystallized perovskite PZ emerged upon heat treatment above 500° C. Bands associated with vibrational motions involving mainly lead ions were not observed in the mid-infrared spectral region.

Fig. 4 illustrates the Raman spectra for PZ materials at room temperature after various stages of heat treatment in an air atmosphere. Similarly to the Raman spectral study for PT materials, the measured Raman spectra for PZ materials that were heat treated below 400° C showed no actual Raman bands but only fluorescence bands due to organic species formed during the burning off of the organic components. In

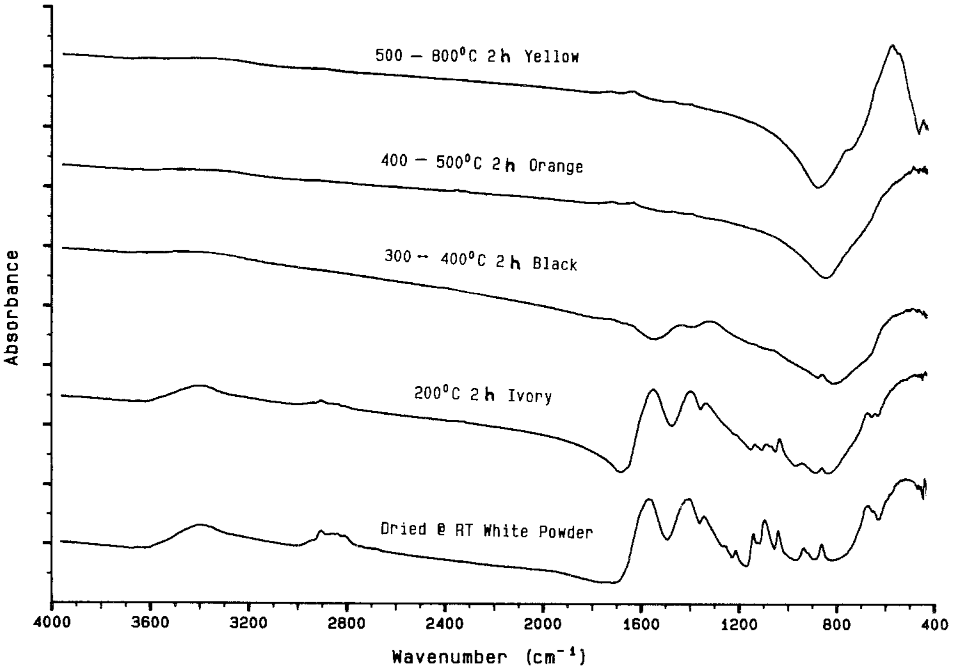


Figure 3 FTIR spectra of heat-treated $PbZrO_3$ materials.

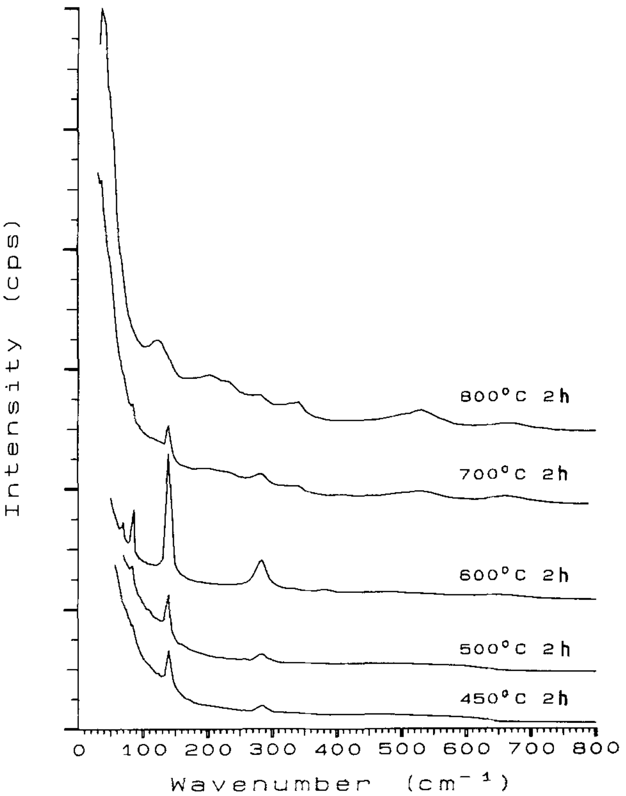


Figure 4 Raman spectra of heat-treated $PbZrO_3$ materials.

contrast to the study for the PT materials, Raman bands were noted for PbO as an intermediate phase when the PZ samples were last treated at 450 to 700° C in an air atmosphere. Raman bands for ZrO_2 were also detected in the Raman spectra for the sample heat treated at 500° C. Samples heated at 700° C showed mixtures of phases containing $PbZrO_3$. Raman spectra of samples heat treated at 800° C or higher showed only the Raman bands of $PbZrO_3$. The perovskite $PbZrO_3$ phase occurred at a higher crystallization temperature during its sol–gel process than the perovskite $PbTiO_3$ phase. Clearly, heat-treatment conditions (temperature and time) played an important role in the crystallization process. If the heat-treatment time was increased to 6 h at ~ 500° C, very strong Raman bands were observed due to monoclinic ZrO_2 and orthorhombic PbO. The observed bands for the sol–gel prepared $PbZrO_3$ materials were shifted from those observed by Pasto and Condrate for a single crystal of $PbZrO_3$ [3, 4]. Similarly to those for sol–gel prepared $PbTiO_3$, these band shifts were probably due to stress effects from the stresses in the polycrystalline material that were generated during the sol–gel preparation [1]. The phase transformations noted on the basis of Raman spectra were consistent with those determined from the powder X-ray diffraction data. However, the X-ray diffraction data also indicated the formation of metallic lead when the PZ material was heat treated at 400° C in an air atmosphere. This phase was not detected using the vibrational spectra. Apparently, the $PbZrO_3$ material underwent intermediate phase separation during its sol–gel preparation in an air atmosphere (forming crystalline ZrO_2 and metallic lead, and then PbO) which did not occur during the sol–gel preparation of $PbTiO_3$ under similar conditions of preparation. Possibly, this difference occurred because of two reasons. First, the preparation of the perovskite PbTiO3 occurred at a lower temperature. Also, titanium ions in the PT materials could possibly possess a convenient variable valence (Ti^{3+} and Ti^{4+}) during the intermediate heat-treatment stages that could counteract the reducing effects when the organic components were being burned off. Heat treatment in a flowing oxygen atmosphere along with agitation during all stages of the sol–gel process should minimize such phase separation for PZ materials. The external modes for a PZ material that was sintered at a lower temperature (800° C for 6 h) convoluted as a broad band centred at 36 cm^{-1}. These external modes would have been resolved if the sample had been heat treated at higher temperatures (900° C for 3 h).

3.4. *In situ* Raman spectra of heat-treated samples at high temperatures

The *in situ* Raman spectra were measured for a pressed powder pellet of sol–gel prepared $PbZrO_3$ at various temperatures through the Curie point (~ 230° C). As expected by group theory, Raman bands decreased in intensity as the Curie temperature was approached. However, the Raman bands did not completely disappear when the sample was heated above the Curie temperature. This result was in contrast to earlier Raman spectral observations for a stoichiometric $PbZrO_3$ single crystal prepared by a conventional melting method [3, 4]. Also, bands for sol–gel prepared perovskite $PbTiO_3$ disappeared through the Curie temperature when measuring at typical signal/noise levels [1]. Possibly, local nonstoichiometry and cation vacancies might have developed in the sol–gel prepared $PZrO_3$ crystals due to preparation conditions that did not occur for the latter materials. As mentioned earlier, phase-separated products (metallic lead, PbO and ZrO_2) were observed during the intermediate stages of heat treatment for PZ materials which were not observed for PT materials. These intermediate phases also had to react in the sol–gel process to form the resulting perovskite $PbZrO_3$ material, possibly causing local nonstoichiometry and cation vacancies during the formation of its crystals. The applied crystallization temperatures were lower than those used for the conventionally prepared $PbZrO_3$ [3, 4]. This interpretation was consistent with the observation of broader Raman bands for the resulting sol–gel prepared $PbZrO_3$ material than for the earlier investigated stoichiometric $PbZrO_3$ crystal [3, 4]. The *in situ* Raman spectra of a sintered $PbZrO_3$ pellet at various temperatures through the Curie temperature showed broad convoluted Raman bands that related to those for the pressed powder pellet. Their observed temperature behaviour was consistent with that for the pressed powder pellets. Strong soft mode behaviour was not detected for the observed Raman bands of the sol–gel prepared $PbZrO_3$ material [5–9]. Small band shifts were observed for the bonds at ~ 45 and 130 cm^{-1} with various illustrated temperature changes. A similar result was observed in the earlier Raman spectral observations for the single crystals of $PbZrO_3$ [3, 4].

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