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Polymerized Complex Synthesis of Perovskite Lead Titanate at Reduced Temperatures: Possible Formation of Heterometallic (Pb,Ti)-Citric Acid Complex

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Perovskite $PbTiO_3$ powders were prepared by a polymerized complex technique at relatively low temperatures, viz. 400−600 °C. Heating of a mixed solution of citric acid (CA), ethylene glycol (EG), and Pb and Ti ions with a molar ratio of Pb/Ti/CA/EG = 1/1/10/40 at 130 °C produced a yellowish transparent polymeric gel without any precipitation, which after pyrolysis at 300 °C was converted to a powder precursor for $PbTiO_3$. We suggest, based on the results of Raman and ^{13}C NMR spectroscopies, that a heterometallic (Pb,Ti)−CA_3 chelate complex formed in a starting Pb/Ti/CA/EG solution and it was thermally stable upon polymerization at 130 °C. Chemical analyses showed no PbO loss during calcination of powder precursors at 400−700 °C, which led to the conclusion that a solid-state reaction between isolated PbO and TiO_2 particles was not responsible for $PbTiO_3$ formation, but $PbTiO_3$ formed directly by thermal decomposition of the powder precursor above 400 °C.

Introduction

Perovskite $PbTiO_3$ is an important ceramic widely used in the electronic industry because of its characteristic ferroelectric, piezoelectric, and pyroelectric properties.[1] The traditional way of preparing $PbTiO_3$ powders based on the solid-state reaction route involves a mixed-oxide process which requires mixing PbO and TiO_2 using ball-milling followed by calcination of the resulting mixture at relatively high temperatures (≥600 °C).[2] One serious problem in processing $PbTiO_3$ (and related Pb-based perovskite materials) by the traditional solid-state reaction route is the severe loss of PbO due to its significant vapor pressure at the processing conditions.[3] The present study has indeed shown that a large PbO loss occurs during calcination of a powder mixture of PbO and TiO_2 already at 600 °C for 2 h. Recently, the PbO loss during rapid thermal annealing of $PbTiO_3$ films has been investigated by Sato et al.,[4] who have demonstrated that the films start to lose PbO significantly during annealing at 600 °C for 60 s. It has then been postulated that the loss of PbO leads to the formation of a parasitic pyrochlore phase generally depleted in PbO compared to the perovskite phase.[5] Formation of the pyrochrore phase is a significant obstacle to the development of high-quality Pb-based perovskite materials, as it can reduce the expected dielectric constant quite severely.[4,6,7] It is thus necessary to compensate the PbO loss during the high-temperature heat treatment by using a starting powder with an excess PbO of an empirically determined amount. Although a pure perovskite $PbTiO_3$ can be prepared in this way, undesired pollution by the toxic PbO is unavoidable.

For this reason, several alternatives based on wet chemical routes, which make possible to lower the synthetic temperature, are becoming increasingly important. These include sol−gel,[8−19] coprecipitation,[15,20−23]

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hydrothermal,[24,25] and polymeric precursor[26,27] methods. Of these, the sol−gel technique utilizing a heterometallic alkoxide with a stoichiometric Pb/Ti = 1 ratio as a molecular precursor for $PbTiO_3$ has received considerable attention,[9−14,17,18] since the heterometallic alkoxide can be hydrolyzed with a controlled amount of water as if it is a single molecule rather than the individual alkoxide mixture, thereby favoring the formation of a multicomponent gel with mixed metal oxygen bonds of −Pb−O−Ti−. This molecular route has therefore facilitated the subsequent formation of pure perovskite $PbTiO_3$ by heating the gel at reduced temperatures (400−600 °C). A major disadvantage of this process, however, is that the heterometallic alkoxide precursor solution is extremely sensitive to moisture and has to be processed under a dry and inert atmosphere. We were therefore interested in exploring another route that enabled the low-temperature (400−600 °C) processing of perovskite $PbTiO_3$ with no need to work under inert atmosphere.

In this work, we present a simple Pechini-type polymerized complex route,[26,28] based on polyesterification between citric acid (CA) and ethylene glycol (EG) that has been successfully used to synthesize perovskite $PbTiO_3$ at 400−600 °C. The advantages of the polymerized complex method include (i) the Pb/Ti/CA/EG precursor solution obtained is much less moisture-sensitive, which means that neither work under dry condition nor perfect removal of waters from solvents is required, and (ii) the technique involves only simple procedures eliminating steps such as careful control of hydrolysis and fine control of pH as usually required for sol−gel techniques. Despite these merits, only little is known about Pb−Ti species involved in the precursor solution. A preliminary Raman spectroscopic work by the present authors has shown that there to be evidence for the presence of a (Pb,Ti)−heterometallic−CA complex in the Pb/Ti/CA/EG precursor solution.[27] The primary goal of this paper is to obtain further evidence for formation of the presumed (Pb,Ti)−heterometallic−CA complex by using Raman and ^{13}C NMR spectroscopic techniques. An important aspect of this technique in the synthesis of $PbTiO_3$ is that such a (Pb,Ti)−heterometallic−CA complex can be immobilized in a rigid polyester network. Immobilization of the heterometallic complex in a rigid polymer can largely reduce segregation of a particular metal during pyrolysis of the polymer. The contiguous ions of lead and titanium in a pyrolyzed product can therefore react with each other with a minimum of diffusion at relatively low temperatures (400−600 °C) to form homogeneous and stoichiometric lead titanate. These temperatures are low enough to avoid the volatilization of lead oxide during calcination and high enough to fully crystallize the perovskite $PbTiO_3$ phase.

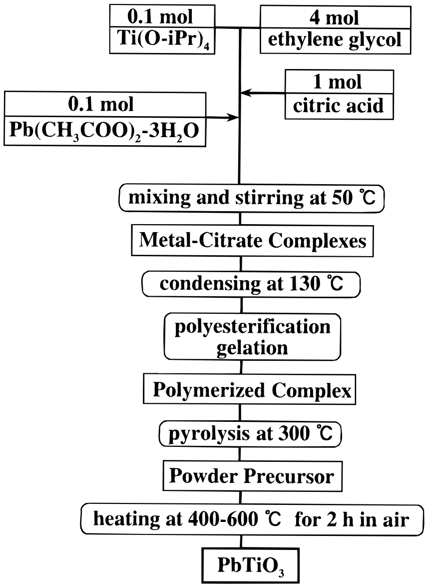

Figure 1. Flowchart for preparing $PbTiO_3$ by the polymerized complex method. The molar ratio of $Ti(OiPr)_4/Pb(CH_3COO)_2\cdot 3H_2O$/citric acid/ethylene glycol = 0.1/0.1/1/4.

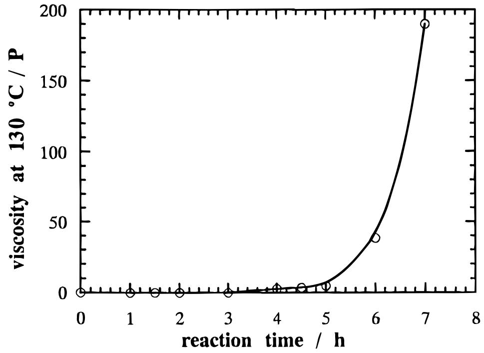

Figure 2. Viscosity of CA/EG solutions with Pb and Ti ions at 130 °C as a function of reaction time.

Experiment

(1) Synthesis of $PbTiO_3$ Powders from the Pb−Ti Precursors. $PbTiO_3$ powders were synthesized by the polymerized complex method as summarized in Figure 1. 0.1 mol of titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, $Ti(O^iPr)_4$; Seimi Chemical Co., Inc. Chigasaki, Japan) was first dissolved into 4 mol of ethylene glycol ($C_2H_6O_2$, EG; E. Merck, Darmstadt, Germany), and subsequently 1 mol of anhydrous citric acid ($HOOCCH_2C(OH)(COOH)CH_2COOH$, CA; Wako Pure Chemical Ind. Ltd., Osaka, Japan) was added in this solution. After achieving complete dissolution, 0.1 mol of $Pb(CH_3COO)_2\cdot 3H_2O$ (Kanto Chemicals Co., Inc., Tokyo, Japan) was added, and the mixture was stirred for 2 h at 50 °C until it became transparent. The colorless clear solution thus obtained was heated at ∼130 °C to promote polymerization and remove excess solvents. With continued heating at ∼130 °C, the solution became more viscous with a change in color from colorless to deep yellow. Noteworthy is that no visible formation of precipitation or turbidity has been observed during the polymerization. The viscosity of the solution at ∼130 °C is shown as a function of reaction time in Figure 2. There was a slow increase in viscosity over 5 h and an abrupt increase

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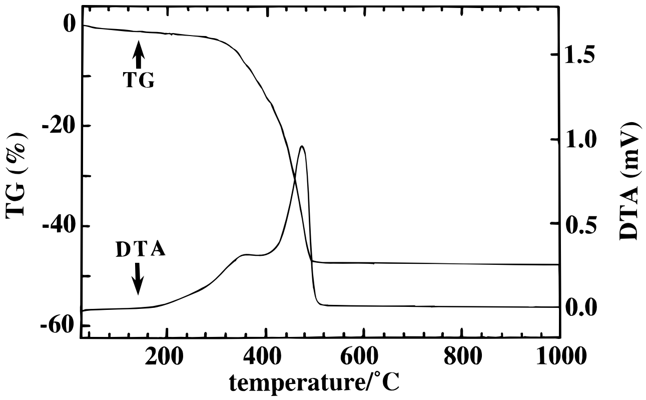

Figure 3. TG-DTA curves of the Pb,Ti precursor in air with a heating rate 10 °C/min.

in viscosity, indicating gelation was observed after 5 h. The resulting gel was a transparent brown resin. Charring the resin at 300 °C for 2 h in an electric furnace resulted in a black solid mass, which was lightly ground into a powder with a Teflon rod. The powder thus obtained is referred to as the "powder precursor" hereinafter. The powder precursor was heat-treated at 400−600 °C for 2 h in static air on an Al_2O_3 boat followed by natural furnace cooling to room temperature. The final powder thus formed showed a light yellow color.

(2) Characterization of Solutions and Powders. Raman spectra at room temperature and ^{13}C NMR spectra at 50 °C were recorded of various solutions at different stages in the preparation in order to obtain information not only on the structure of complex species in the initial precursor solutions but also on the thermal stability of the complex. The Raman spectra were recorded with a Perkin-Elmer system 2000R FT-Raman spectrometer. A standard Fourier transform NMR spectrometer (JEOL, NMR-GSX-270, Japan) operating at 67.9 MHz of a ^{13}C resonance frequency was used. The sample solutions were transferred to a 10 mm diameter NMR tube, and inside this tube was coaxially placed a 3 mm-diameter capillary tube containing a deuterated lock solvent (D_2O). Tetramethylsilane (TMS) was used as a reference for reported ^{13}C chemical shifts; i.e., the resonance position of the methyl carbon of TMS was set to 0 ppm.

Thermogravimetry−differential thermal analysis (TG-DTA; Type-2020, MAC Science Co., Japan) was carried out to follow the decomposition and crystallization of precursors with a heating rate of 10 °C/min in static air up to 1000 °C. X-ray diffraction (XRD; MXP^{3VA}, Cu Kα, 40 kV, 40 mA, MAC Science, Japan) of the various powders was carried out with a scan rate of 4° (2θ)/min for phase identification.

To check if PbO loss has occurred during the heat treatment, Pb/Ti ratios in polymerized complex Pb/Ti powders calcined in air at 400−700 °C for 2 h were determined by ICP (inductive coupled plasma) analysis. For comparison, Pb/Ti ratios in mixed powders of PbO and TiO_2 (initially with Pb/Ti = 1.00) heat treated in air at 400−600 °C for 2 h were also determined. The carbon content in the polymerized complex Pb/Ti powder calcined in air at 400 °C for 2 h was determined to be 0.47 wt % by the coulometric titration technique. Contents of carbons decreased down to ~0.2 wt % level either by increasing the heat treatment time up to 8 h at 400 °C or by calcining the precursor at 500 °C for 2 h. Calcinations at temperatures higher than 600 °C resulted in almost complete elimination of carbons.

Results and Discussion

(a) Structural Evolution of Perovskite $PbTiO_3$. Figure 3 illustrates typical TG-DTA curves of a Pb−Ti powder precursor fired in air. The TG curve indicates that the weight loss occurred rather continuously, it was completed by 480 °C for a heating rate of 10 °C/min, and that above 480 °C there was no further weight loss up to 1000 °C. Any clear plateaus, indicating formation of well-defined intermediate decomposition products, were not identified on the TG curve. The DTA result in Figure 3 revealed two exotherms at approximately 350 and 460 °C. From 200 to 400 °C the reactions were mildly exothermic, which were associated with the initial stage of decomposition of the organic species involved in the powder precursor. A sharper exotherm peak was observed at 460 °C corresponding to the larger weight loss observed by TG between 400 and 480 °C which was attributed to complete burnout of the residual organics. In the temperature region of increasing negative slope on the TG curve between 400 and 480 °C, the decomposition of the powder precursor accompanied drastic crystallization of the perovskite $PbTiO_3$ as revealed by XRD (Figure 4). In view of the fact that there is no further thermal events above 480 °C up to 1000 °C, it can be concluded that no PbO loss has occurred once $PbTiO_3$ formed.

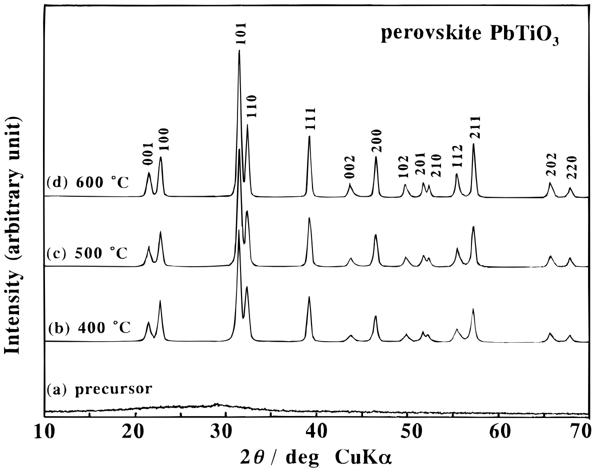

Figure 4. XRD patterns of the Pb,Ti precursor (a) and the calcined powders in air for 2 h at 400 (b), 500 (c), and 600 °C (d).

The XRD patterns of the starting powder precursor and of powders obtained after calcining the powder precursor in air at different temperatures for 2 h are shown in Figure 4 in a 2θ range of 10−70°. The starting powder precursor was primarily amorphous in structure, as shown by the broad continuum in the XRD in Figure 4a. Drastic crystallization has occurred during the heat treatment of the powder precursor in air at 400 °C for 2 h (Figure 4b). The width of the principal lines somewhat sharpens at 500 °C (Figure 4c) and 600 °C (Figure 4d) but the overall shape of the pattern remains unchanged. The XRD patterns in Figure 4b−d exhibited a pure tetragonal phase of $PbTiO_3$ with a perovskite structure. Of particular importance is that no reflections from foreign phases, such as pyrochlore $Pb_2Ti_2O_6$ or PbO-depleted pyrochlore phases, orthorhombic PbO, tetragonal PbO, orthorhombic PbO_2, or TiO_2 were observed. It should be mentioned here that the heat treatment at 400 °C with reaction times much shorter than 2 h would be insufficient for the full crystallization, since the TGA with 10 °C/min (Figure 3) showed a significant weight loss above 400 °C. Note also that the calcined powders at 400 °C for 2 and 8 h contained residual carbons in amounts of 0.47 and 0.21 wt %, respectively (see Experimental Section). ICP chemical analyses have shown that no significant deviation from the stoichiometry (Pb/Ti = 1.00) was observed for the polymerized complex powders calcined at tem-

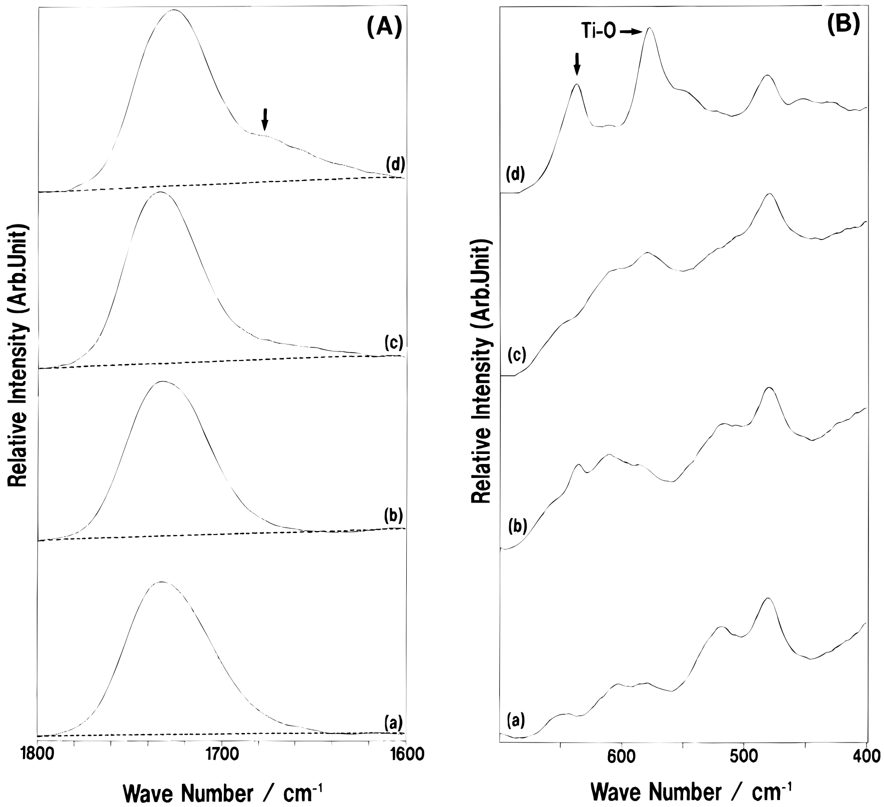

Figure 5. FT Raman spectra of CA/EG solutions without metal ions (a) and with 0.2 mol of Pb (b), 0.2 mol of Ti (c), and equimolar (0.2 mol) Pb and Ti (d) in the COOH (A) and Ti−O (B) vibrational frequency region; CA/EG = 1/4 and CA/Pb (or Ti) = 5. Dotted lines connecting both ends of each spectrum at 1800 and 1600 cm^{-1} may be used as a guide for notifying the characteristic bump shown by an arrow on (d).

peratures ranging from 400 to 700 °C. In contrast, significant Pb losses in amounts of 2% (Pb/Ti = 0.98) and 12% (Pb/Ti = 0.88) occurred when a mixed powder of PbO and TiO_2 was heat-treated in air at 500 and 600 °C for 2 h, respectively. These results would in turn indicate that a solid-state reaction between isolated PbO and TiO_2 particles was not responsible for $PbTiO_3$ formation, but instead $PbTiO_3$ formed directly by thermal decomposition of the X-ray amorphous polymerized complex precursor above 400 °C. The success in lowering the synthetic temperature to ~400 °C can probably be connected with possible formation of a Pb−Ti heterometallic CA complex, the results of which are shown below.

(b) Solution Characterization. Figure 5 shows selected regions of FT Raman spectra of CA/EG solutions without metal ions (a), containing lead ions (b), titanium ions (c), and equimolar lead and titanium ions (d). Here we focus our attention on only two selected frequency regions that are worth discussing, i.e., the 1800−1600 cm^{-1} (A) and 800−400 cm^{-1} (B) regions, related to COOH and Ti−O vibrations, respectively. The intense band at 1730 cm^{-1} observed for all the solutions can be assigned to the carbonyl C=O stretching mode in the −COOH carboxylic acid groups of CA.[29] Because of the large excess of CA relative to Pb or Ti ions (mole ratio of CA/Pb (or Ti) is 5 in this case), most of the intensity of the 1730 cm^{-1} band comes from −COOH not directly bound to metals. A weak but significant shoulder at a lower frequency side of the 1730 cm^{-1} Raman band for the Ti−CA/EG solution is responsible for the formation of a titanium−CA chelate complex.[30,31] An interesting result now emerges in the COOH region of the FT Raman spectrum of the (Pb,Ti)−CA/EG solution (Figure 5A(d)), where a shoulder of the 1730 cm^{-1} band (marked with ↓) gained much more intensity than expected from a simple combination of the individual Pb−CA/EG and Ti−CA/EG spectra. Similarly, the spectral features in the Ti−O stretching region[32] for both the Ti−CA/EG and the (Pb,Ti)−CA/EG solutions differ greatly with each other in the band envelope and intensity. Again the latter spectrum (Figure 5B(d)) is not composed of two individual Raman spectra of Pb−CA/EG (Figure 5B(b)) and Ti−CA/EG (Figure 5B(c)) solutions. These findings would suggest that lead and titanium ions have a strong interaction during the chelation presumably to form a heterometallic CA complex in a way similar to what has been found in (Ba,Ti)−CA/EG solutions.[30,31] This is further substantiated by measuring ^{13}C NMR spectra of these solutions, as shown below.

Figure 6 shows a selected region of ^{13}C NMR spectra of CA/EG solutions without metal ions (a), containing Pb ions (b), Ti ions (c), and both Pb and Ti ions in equal amounts (d), where resonance signals marked with ○

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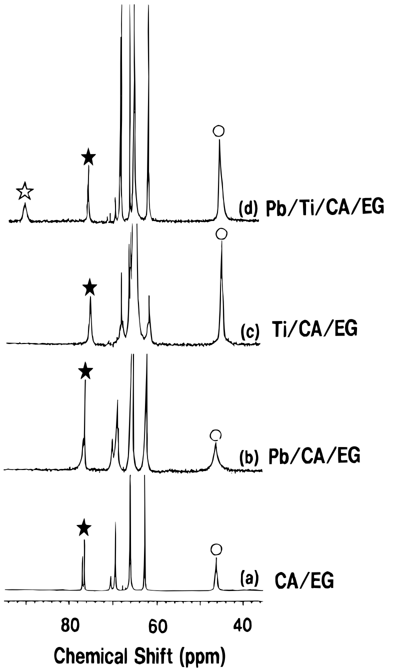
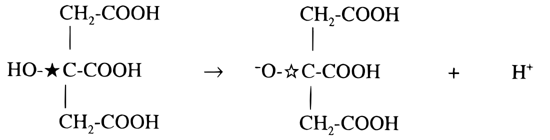


Figure 6. ^{13}C NMR spectra of CA/EG solutions without metals (a) and with 0.2 mol of Pb (b), 0.2 mol of Ti (c), and equimolar (0.2 mol) Pb and Ti (d) measured at 50 °C; CA/EG = 1/4 and CA/Pb (or Ti) = 5. Chemical shifts are scaled with the TMS (tetramethylsilane) standard.

and ★ are due to methylene (46 ppm)[33] and alcoholic carbons (78 ppm)[33] in CA or esterificated CA,[34] respectively, while a numerous number of resonance peaks in a 62−72 ppm region correspond to methylene carbons in unreacted EG[33] or a variety of esterificated EG species.[35] The most striking result is that the simultaneous presence of Pb and Ti ions in the CA/EG solution gives rise to a new resonance at 91 ppm (☆) in addition to the resonance at 78 ppm associated with the alcoholic carbon (★) of CA (Figure 6d). According to the magnitude of the chemical shift, the new peak at 91 ppm (☆) can be assigned to the central carbon in CA with dissociation of the proton from the hydroxy group which bonds to the same carbon (hereinafter we refer this carbon to "*de*protonated alcoholic carbon"):[30,31]



$$\begin{array}{c} CH_2\text{-}COOH \\ | \\ HO\text{-}\bigstar C\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{array} \rightarrow \begin{array}{c} CH_2\text{-}COOH \\ | \\ {}^-O\text{-}\star C\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{array} + H^+ \qquad (1)$$

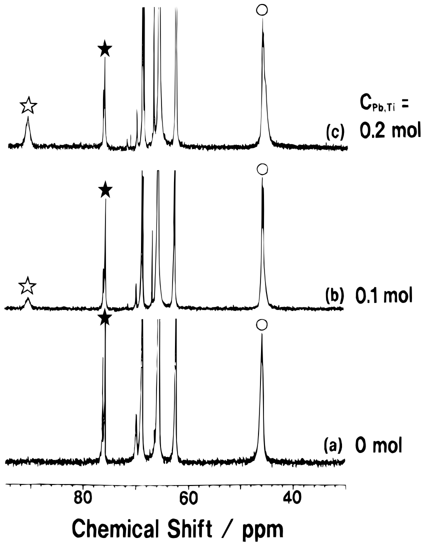


Figure 7. ^{13}C NMR spectra of CA/EG solutions containing equimole of Pb and Ti ions measured at 50 °C; $C_{Pb,Ti}$ = 0 (a), 0.1 mol (b), and 0.2 mol (c) relative to 1 mol of CA and CA/EG = 1/4. Chemical shifts are scaled with the TMS (tetramethylsilane) standard.

The fact that this type of resonance has been observed exclusively in solutions containing Pb and Ti ions in equal amounts would indicate the formation of another type of complex different from those present in the Pb−CA/EG or Ti−CA/EG solutions. A linear increase in the relative intensities of the 91 ppm peak with increasing a total amount of Pb and Ti, which is accompanied with a linearly decreased intensity of the feature around 78 ppm,[36] may imply that the peak at 91 ppm is attributable to a given complex unique to the (Pb/Ti)−CA/EG solution, while the 78 ppm feature to excess free CA (or esterificated CA) rather than to the CA coordinating to metals (Figure 7). Let us suppose the (Pb/Ti)−CA/EG solution to contain a heterometallic CA complex, (Pb,-Ti)−(CA)$_n$, as a main species, wherein both the lead and titanium ions are stabilized simultaneously with CA. It is probable that the *de*protonated alcoholic $-\mathbf{C}-\mathbf{O}^-$ group in CA (responsible for the 91 ppm peak) as well as other carboxylic acid −**COOH** groups plays a key role to stabilize such a heterometallic complex, as the former should have a very strong affinity to metal ions.[37] In a manner similar to the ^{13}C NMR spectroscopic analysis performed for (Ba/Ti)−CA/EG solutions,[30,31] a linear relationship between $C_{Pb,Ti}$ (the known amount of Pb or Ti) and C_{C-O^-} (the amount of *de*protonated $-\mathbf{C}-\mathbf{O}^-$ group in CA) was exploited to evaluate the number of CA participating in the complex formation. C_{C-O^-} was calculated from the total amount of CA and the values of $I_{C-O^-}/(I_{C-OH} + I_{C-O^-})$ experimentally determined from the ^{13}C NMR spectra shown in Figure 7, where I_{C-O^-} and I_{C-OH} correspond to the respective integrated intensities of the 91 ppm signal (*de*protonated alcoholic carbon in CA) and of the 78 ppm signal (the parent alcoholic carbon in CA) normalized to a total intensity of the 46 ppm CH_2 carbon signal in all species derived from CA. On the assumption that only CA with *de*protonated $-\mathbf{C}-\mathbf{O}^-$ group participates in the formation of the presumed heterometallic (Pb,Ti)−(CA)$_n$ complex, one can have $n \sim 3$ by the extrapolation of the linear C_{C-O^-} vs $C_{Pb,Ti}$ plot to $C_{Pb,Ti}$ = 1 mol. A similar heterometallic CA complex has been recently found in Ba−Ti−CA−

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(34) The observed peak splitting or broadening is basically due to the esterification between the hydroxyl OH group of EG and the carboxylic acid COOH group of CA, which occurs quite easily during the dissolution process of CA (and starting metal compounds) at 50 °C.

(35) A numerous number of sidebands in addition to the main resonance of EG at ~66 ppm can be assigned to ester carbons or higher order ester carbons resulting from esterification reactions among EG, CA, and their esterificated derivatives.

(36) The *integrated* intensities of ~78 ppm features relative to those of ~46 ppm feature associated with $-CH_2-$ of CA decrease linearly with metal concentration.

(37) Since the ionization described by eq 1 does not significantly occur in solutions free from metals even at very high pH (see: Strouse, J.; Layten, S. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 562), CA with $-\mathbf{C}-\mathbf{O}^-$ group responsible for the resonance at 91 ppm in Figure 6d should be present not as a free ion but as a ligand stabilized through the proposed complex formation of (Pb,Ti)−(CA)$_n$.

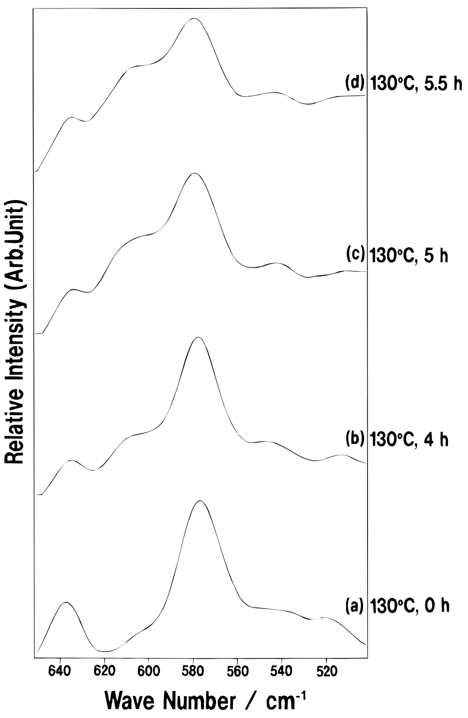

Figure 8. FT Raman spectra of the Ti−O vibrational region for Pb/Ti/CA/EG solutions reacted at 130 °C for 0 h (a), 4 h (b), 5 h (c) and 5.5 h (d). The molar ratio of Pb/Ti/CA/EG = 0.2/0.2/1/4.

EG systems, wherein formation of a complex with a stoichiometry close to Ba/Ti/CA = 1/1/3 was proposed.[30,31]

Figure 8 shows the *n*(Ti−O) region of FT Raman spectra of a series of (Pb/Ti)−CA/EG samples that were prepared by reacting the initial solution at 130 °C for different duration ranging from 0 to 5.5 h. The last sample obtained after the reaction of the longest duration was of resin form at room temperature. The characteristic Raman band at 580 cm^{-1}, which was assigned to Ti−O vibrations in the heterometallic CA complex, was observed without any noticeable change in its position for all the solutions studied even after the solution was gelatinized to form a solid resin.[38] This strongly suggests that the presumed heterometallic CA complex is thermally stable upon polymerization at 130 °C and the basic coordination structure remains almost unchanged in the polymeric resin. It is tempting to state here that the formation of such a stable (Pb,Ti)−CA$_3$ complex and the maintenance of its atomic scale mixing during the course of polymerization would be one of the most important factors for achieving complete atomic mixing of Pb and Ti in the pyrolyzed product, thus lowering the processing temperature for perovskite PbTiO$_3$ down to ~400 °C. Currently, isolation of this heterometallic complex from solutions into a crystalline form is under way to provide more convincing evidence for the proposed stoichiometry.

Conclusion

It was supposed by Raman and ^{13}C NMR spectroscopic techniques that a starting (Pb,Ti)−CA/EG precursor solution contained a heterometallic (Pb,Ti)−CA$_3$ complex which was thermally stable at 130 °C upon polymerization. A pure perovskite PbTiO$_3$ free from Pb$_2$Ti$_2$O$_6$ pyrochlore or PbO depleted pyrochlore phases has been successfully synthesized by heat-treating the polymerized complex precursors in air at 400−600 °C for 2 h.

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[38] Evolution of a new broad feature around 610 cm^{-1} with reaction time is connected with an increased number of ester bonding in CA/EG mixtures.