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# $PbTiO_3$ sol–gel process studied by $^{207}$Pb-NMR, IR, DTA and XRD

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$PbTiO_3$ film and powder materials have been obtained from a sol prepared at room temperature by mixing lead(II) acetate trihydrate (LAT) and tetraisopropylorthotitanate (TPOT) in methoxyethanol. The sol–gel process was studied by means of $^{207}$Pb nuclear magnetic resonance and infrared spectroscopy, differential thermal analysis and X-ray diffraction measurements. This investigation shows that an interaction between LAT and TPOT occurs immediately on mixing in solution and, as a result of the interaction, the lead and titanium compounds are indistinctly linked together through bidentate acetate bridging. This linkage remains unchanged during solution reactions and gelation, Pb–O–Ti bonding being absent at this stage. Pb–O–Ti bonding in the sol–gel materials is believed to be first formed between 200 and 350 °C during the decomposition of the OAc group of LAT and its removal from the gel. The gel retains its amorphous state on heating at 370 °C for 1 h. An unidentified primary crystal phase appears after heating the gel at 400 °C for 1 h, and it is transformed into perovskite $PbTiO_3$ crystals at 500 °C and higher temperatures.

## 1. Introduction

The sol–gel processing of glasses and ceramics has generated considerable interest, but most of the work in the past has been concentrated on the amorphous materials in the silica system. In recent years, there has been an increasing trend towards the fabrication of materials in other systems with special optical, electrical and other interesting properties. The $PbO–TiO_2$ sol–gel system is one which has attracted much attention, and the preparations of many sol–gel materials have been reported [1–6].

When dealing with the $PbO–TiO_2$ sol–gel system, generally, lead(II) acetate trihydrate (LAT) and tetraisopropylorthotitanate (TPOT) are chosen as starting materials, chemical modifications being made by a refluxing process between 85 and 125 °C before the final sol–gel solution is obtained [6]. Recently, we prepared stable $PbO–TiO_2$ sol–gel solutions in a wide composition range by mixing the two starting materials with solvent and catalyst at room temperature without using the fluxing process, and from these solutions both ceramic powders and dip-coating films were obtained. The present work studies the sol–gel process of $PbTiO_3$ materials. It was revealed that during the solution and gelation processes, the lead and titanium compounds are linked together through bidentate acetate bridging and not through Pb–O–Ti bonding. It is suggested that the Pb–O–Ti bonding is formed during heat treatment of the gel between 200 and 350 °C.

## 2. Experimental procedure

The starting materials are lead(II) acetate trihydrate (LAT) and tetraisopropylorthotitanate (TPOT). Methoxyethanol (MOE) and hydrochloric acid (HCl) were chosen as solvent and catalyst. A homogeneous, clear and stable solution with the composition of 50 mol % LAT and 50 mol % TPOT was prepared at room temperature by mixing the methoxyethanol solutions of LAT and TPOT in the presence of HCl. The solution is referred to here as TP50.

$^{207}$Pb nuclear magnetic resonance (NMR) spectra were taken by using a CXP200 B NMR spectrometer at room temperature. All the chemical shifts of $^{207}$Pb are reported relative to tetramethyllead $Me_4Pb$ ($\delta = 0$), and lead nitrate $Pb(NO_3)_2$ ($\delta = -2960$ p.p.m.) [7] was used as an external standard.

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Differential thermal analysis (DTA) of room-temperature dried gels was carried out under flowing air and nitrogen with scan rate of 10 °C min$^{-1}$ on a Perkin–Elmer DTA1700. Samples used for infrared (IR) and X-ray diffraction (XRD) analyses were prepared by heating TP50 gels at different temperatures ranging from 100–800 °C for 1 h. Infrared spectra of the samples were taken by using a Nicolet 5PC FT–IR spectrometer over the wave number range 400–4000 cm$^{-1}$. The KBr pellet method was employed. X-ray measurements were performed with a Philips PW 1050 Powder Diffractometer, using Cu$K_\alpha$ radiation.

## 3. Results and discussion

From TP50 solution, only one $^{207}$Pb-NMR signal around −883 p.p.m has been found in a very wide range from −3600 to −300 p.p.m. This peak is observed immediately on mixing the lead and the titanium compounds in solution, and it remains unchanged with time even during the gelation process, see Fig. 1b–d. Compared with the simple lead acetate in methoxyethanol, which has a $^{207}$Pb-NMR signal with the peak at −1248 p.p.m (see Fig. 1a), there is a big up-field shift of $^{207}$Pb-NMR signal in TP50. This indicates that an interaction between lead acetate and the titanium compound has happened very quickly in the solution, and a new chemical environment regarding the lead atom has established. However, $^{13}$C and $^{1}$H NMR spectra of freshly prepared TP50 solution samples show that neither the –OPr group of the titanium compound nor the –OAc group of the lead compound are changed (the details of this study will be reported elsewhere). So large and rapid $^{207}$Pb-NMR chemical shift of TP50 cannot be explained by the new chemical bond formation, as for example Pb–O–Ti bonding, of the lead compound.

Infrared spectra provide additional interesting information about TP50 sol–gel sample. Fig. 2a shows the IR spectrum of lead acetate trihydrate crystals, which consists of eight peaks in the range 400–2000 cm$^{-1}$. Those associated with COO stretching vibrations are at 1543 cm$^{-1}$ ($\nu_{as}$) and 1414 cm$^{-1}$ ($\nu_s$), and the peak at 663 cm$^{-1}$ is due to the vibration of the Pb–O bond of the compound [8]. From Fig. 2b, one can see that almost all the eight peaks of lead acetate are present in the spectrum of the TP50 gel heat treated for 1 h at 100 °C. This result demonstrates that after solution reactions and gelation, lead acetate still exists in the low-temperature treated TP50 gel. It is noteworthy that the frequency separation of the two COO stretching peaks ($\Delta\nu = \nu_{as} - \nu_s$) is 129 cm$^{-1}$ in lead acetate crystals (Fig. 2a), while that in TP50 is 140 cm$^{-1}$ (Fig. 2b), an increase of 11 cm$^{-1}$. According to many published results of the infrared spectra of metal acetate [8,9], a frequency separation, $\Delta\nu$, between 80 and 160 cm$^{-1}$ indicates the presence of bidentate ligands (while for monodentate acetate the $\Delta\nu$ value is 400–500 cm$^{-1}$), and a larger $\Delta\nu$ in the same range, generally between 120 and 160 cm$^{-1}$, suggests bridging bidentate acetates. Considering the larger $\Delta\nu$ value (140 cm$^{-1}$) of TP50, it is quite possible that the acetyl group of lead acetate in the sol–gel samples acts as a bridging bidentate.

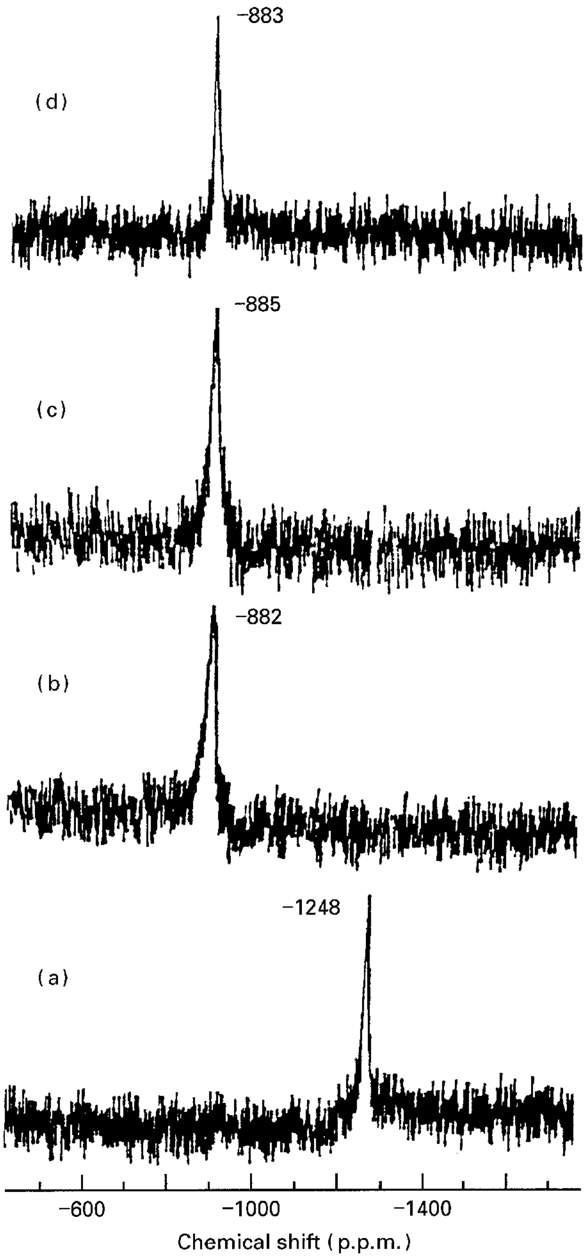


*Figure 1* $^{207}$Pb-NMR spectra of lead acetate trihydrate in (a) methoxyethanol, (b) freshly prepared TP50 solution, (c) TP50 solution aged for 30 days and (d) just gelled TP50 sample. $^{207}$Pb-NMR chemical shifts are reported relative to that of $PbMe_4$ ($\delta = 0$).

From NMR spectra (Fig. 1), we have seen that there is a rapid interaction between TPOT and LAT in solution. The linkage between them, established as a result of the interaction, is stable and remains unchanged even after gelation. On the other hand, the IR characteristics of lead acetate compound do not change greatly in TP50 gel (Fig. 2), and the only prominent difference is the increase in the frequency separation of its two COO stretching modes from 129 cm$^{-1}$ to 140 cm$^{-1}$. Based on these results and the above discussion, it is suggested that when LAT is mixed with TPOT in the solution, the two compounds interact quickly forming a kind of linkage or a kind of association through bidentate acetate bridging, which

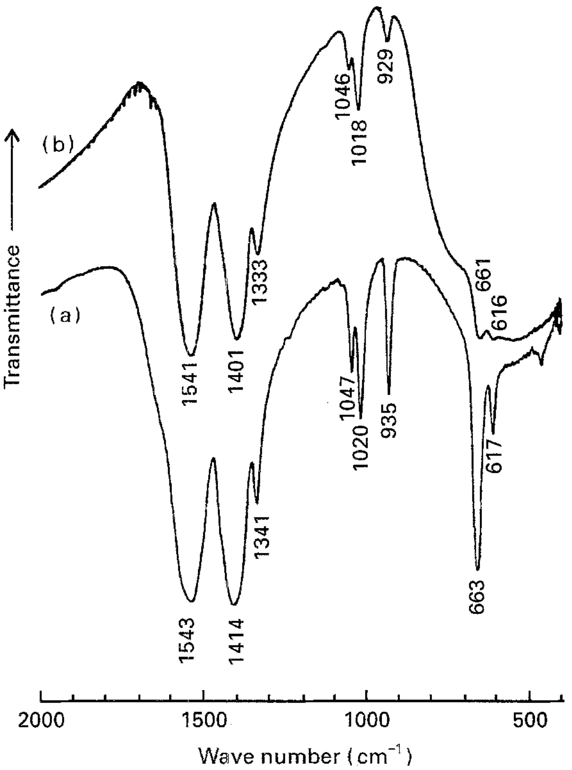
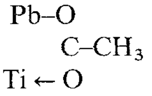


*Figure 2* IR spectra of (a) lead acetate trihydrate crystals and (b) TP50 gel treated at 100 °C for 1 h.

can be described as



$$\begin{array}{l} \text{Pb–O} \\ \qquad \text{C–CH}_3 \\ \text{Ti} \leftarrow \text{O} \end{array}$$

The linkage remains unchanged during solution reactions and gelation. That accounts for the $^{207}$Pb-NMR signal of TP50 samples at −883 p.p.m, which retains the same position, regardless of whether the sample is a freshly prepared solution, an aged solution or one which has just gelled.

Most of the solutions in the $PbO–TiO_2$ system are reported to be made through the refluxing process. Previous studies show that chemical modifications of the starting alkoxide and lead acetate [6, 10, 11] can occur during the process. One gelation mechanism proposed was a transesterification reaction involving Pb–O–Ti bond formation [10, 11]. However, in our case, the gelation process is clearly controlled by a different mechanism, because the Pb–O–Ti bond is not formed during the solution reactions and the gelation process. The difference may be caused by the different sol–gel processing procedures, because we did not employ the high-temperature refluxing process to prepare the parent solution.

Fig. 3 shows the IR spectra of TP50 gels heated at different temperatures for 1 h. The IR peaks related to organic groups are concentrated in the region 900–1700 cm$^{-1}$. Two peaks from lead acetate, occurring at around 660 and 614 cm$^{-1}$, can also be seen, overlayed by a very broad and strong band ranging from 400–800 cm$^{-1}$. All the bands due to organic groups, including those linked with $Pb(OAc)_2$ compound, diminish with increasing temperature, and disappear from the spectrum at 400 °C (see Fig. 3).

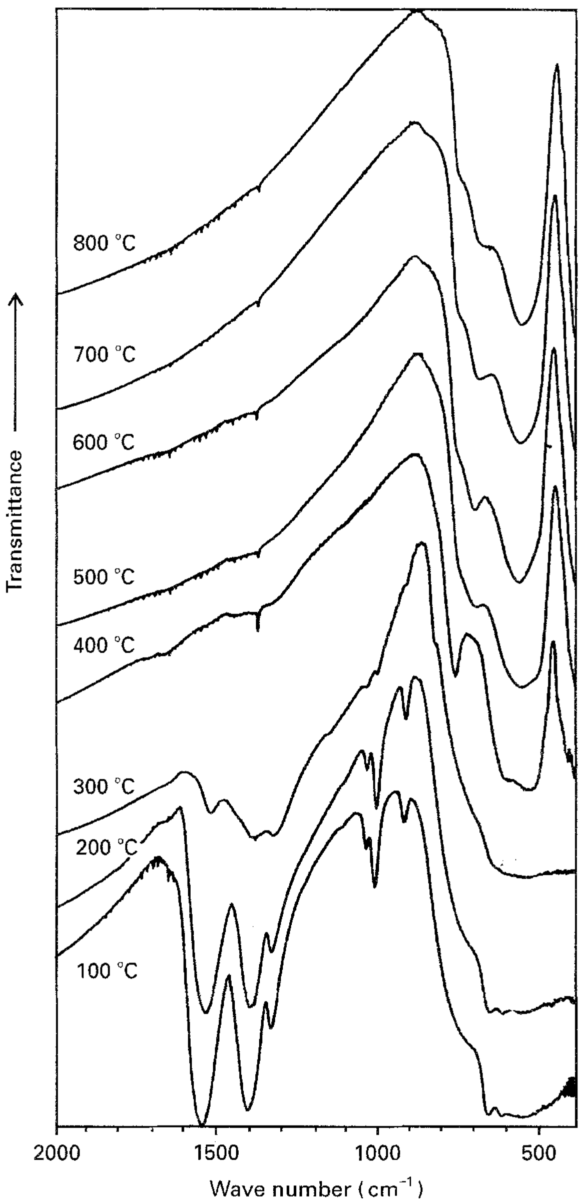


*Figure 3* IR spectra of TP50 treated at different temperatures for 1 h.

For DTA curves, (Fig. 4), one can observe peaks corresponding to residual solvent evaporation at 128 °C, the OAc decomposition near 280 °C (which becomes more prominent under nitrogen), the combustion of organic substances between 340 and 370 °C, and crystallization at 440 and 480 °C. The exothermic peaks due to combustion and crystallization are not present under nitrogen. Some workers have noticed that hydrolysis of bidentate acetates seems to be difficult so that acetate groups still remain in the monolithic xerogel, and are only removed upon heating at a temperature of about 300 °C [12]. This agrees with the results of IR spectra and DTA analysis of our TP50 sample. It is believed that the Pb–O–Ti bonding is formed during the OAc decomposition and its removal from the gel which, according to IR spectra and DTA curves, occurs between 200 and 350 °C.

The very strong and broad IR band at 400–800 cm$^{-1}$ in Fig. 3 shows no significant changes until 400 °C. This band has been observed for many $TiO_2$-rich glasses and the sol–gel derived $TiO_2$

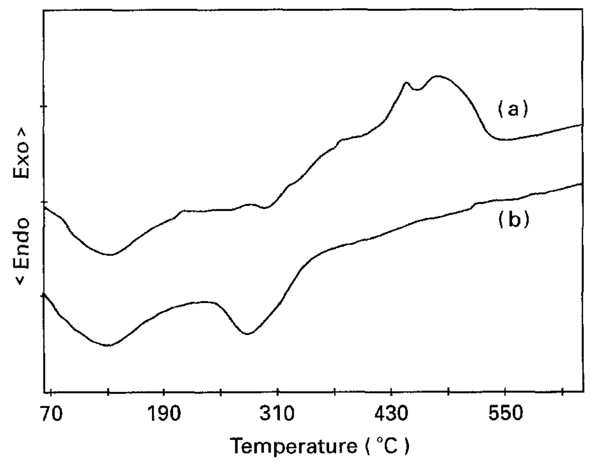


*Figure 4* DTA curves of TP50 gels under flowing (a) air and (b) nitrogen. Scan rate 10.0 °C min$^{-1}$, gas flow 50 cm$^3$ min$^{-1}$.

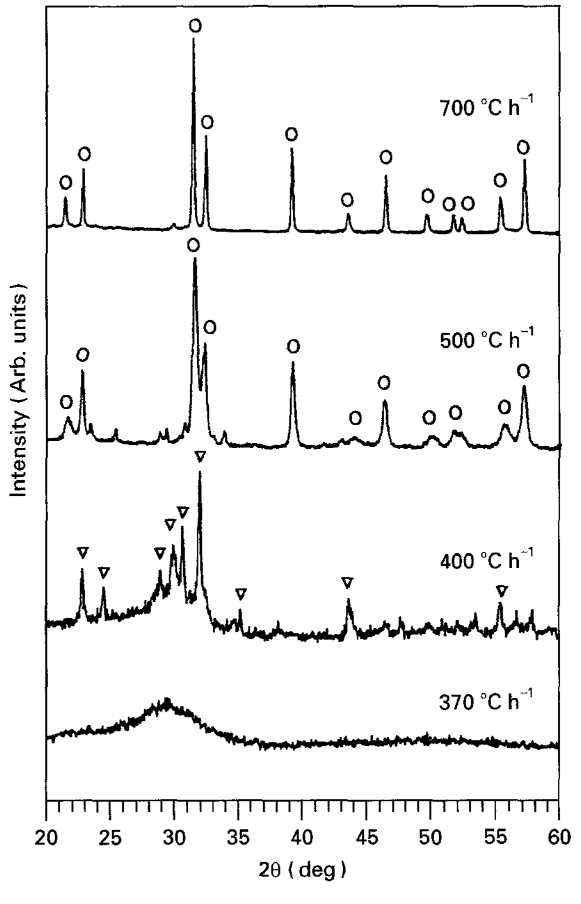


*Figure 5* XRD patterns of TP50 treated at different temperatures for 1 h. (○) Perovskite PbTiO$_3$, (∇) unidentified phase.

containing materials, and is due to the vibration of the Ti–O bond [13, 14]. From 400–800 °C, dramatic changes of this band are observed. It splits into three peaks when the temperature reaches 400 °C, one at 770 cm$^{-1}$, another at 536 cm$^{-1}$ with a shoulder at the higher wavenumber side, and the third one near to but lower than 400 cm$^{-1}$. The appearance of the sharp IR peaks is caused by the crystallization of the gel. At 500 °C, the peak at 770 cm$^{-1}$ disappears, and a new peak at 710 cm$^{-1}$ is observed. This peak shifts to lower wavenumbers with increasing temperature and finally becomes a prominent shoulder on the high wavenumber side of a strong band centred at 571 cm$^{-1}$. The peak at a wavenumber lower than 400 cm$^{-1}$ appears to be unchanged. The corresponding X-ray diffraction spectra (Fig. 5) give clear evidence of the crystallization of the gel. From Fig. 5, one can see that the gel is still amorphous after being treated at 370 °C for 1 h. At 400 °C, an unidentified primary crystal phase appears, which is converted into perovskite PbTiO$_3$ crystals at 500 °C and higher temperatures.

## 4. Conclusions

PbTiO$_3$ formation by a sol–gel process has been studied using $^{207}$Pb-NMR, IR, DTA and XRD spectral data. The study indicates that during the solution and gelation processes of the sol–gel derived PbTiO$_3$ materials, the lead and titanium compounds are probably linked together through bidentate acetate bridging, rather than through Pb–O–Ti bonding. The Pb–O–Ti bonding is believed to be first formed in the temperature range between 200 and 350 °C during the OAc decomposition and its removal from the gel. The gel retains its amorphous state when heated at 370 °C for 1 h. An unidentified primary crystal phase appears on heating the gel at 400 °C for 1 h, and this is transformed into perovskite PbTiO$_3$ crystals at 500 °C and higher temperatures.

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## References

1. K. D. BUDD, S. K. DEY and D. A. PAYNE, in "Better ceramics through chemistry II", edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (Materials Research Society Proceedings 73, Pittsburgh, PA, 1986) pp. 711–16.
2. H. JANSSON, C. E. MILLAR and S. J. MILNE, in "Better ceramics through chemistry IV", edited by B. J. J. Zelinski, C. Jeffrey Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society Proceedings 180, Pittsburgh, PA, 1990) p. 421.
3. J. MARILLET and D. BOURRET, *J. Non-Cryst. Solids* **147/148** (1992) 266.
4. H. DISLICH, in "Sol-gel technology for thin films", edited by L. C. Klein (Noyes, Park Ridge, NJ, 1988) p. 50–79.
5. J. B. BLUM and S. R. GURKOVICH, *J. Mater. Sci.* **22** (1987) 2655.
6. S. D. RAMAMURTHI and A. D. PAYNE, in "Better ceramics through chemistry IV", edited by B. J. J. Zelinski, C. Jeffrey Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society Proceedings 180, Pittsburgh, PA, 1990) p. 79.
7. R. K. HARRIS and B. E. MANN, "NMR and the periodical table" (Academic Press, London, New York, San Francisco, 1978).
8. K. NAKAMOTO, "Infrared and raman spectra of inorganic and coordination compounds", 3rd Edn (Wiley, New York, 1978).

9. K. H. VON THIELE and M. PANSE, *Z. Anorg. Allg. Chem.* **441** (1978) 23.
10. T. W. DEKLEVA, J. M. HAYES, L. E. CROSS and G. L. GEOFFROY, *J. Am. Ceram. Soc.* **71** (1988) C280.
11. S. R. GURKOVICH and J. B. BLUM, in "Ultra structure processing of ceramics, glasses and composites", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984) p. 152.
12. S. DOEUFF, M. HENRY, C. SANCHEZ and J. LIVAGE, *J. Non-Cryst. Solids* **89** (1987) 206.
13. B. E. YOLDAS, in "Ultra structure processing of ceramics, glasses and composites", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984) p. 65.
14. K. A. MAURITZ and C. K. JONES, *J. Appl. Polym. Sci.* **40** (1990) 1401.

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