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Sol–gel derived $PbTiO_3$

Part 2 *Structural control of monolithic gels*

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Lead titanate gels have been prepared by adding an aqueous nitric acid solution to a Pb–Ti complex alkoxide. A systematic study was made to examine the effects of process parameters such as amounts of water and acid alkoxide molarity on the gelation time as well as on the structure of the gels obtained. The gel structure was characterized by the elastic modulus which was determined via sound wave propagation through the gels. It was found that an increase in both the amount of water and alkoxide molarity caused rapid gelation. Acid additions not only suppressed gelation but also reduced the elastic moduli of the resultant gels. Gels having a low elastic modulus were found to be desirable for the suppression of cracking during ageing and drying. Addition of an excessive amount of acid, however, prevented the formation of a large scale polymer-network and resulted in a powder-like gel. The porosity and dielectric constant of dried gels are also reported.

1. Introduction

Recently, sol–gel processing has been recognized as an important technique for forming glass [1–3] and ceramics [4–6]. Sol–gel processing of ceramics contains the following steps [7]:

(a) preparation of an appropriate alkoxide
(b) gel-preparation
(c) ageing and drying
(d) gel-to-ceramic conversion by firing.

One of the most serious problems is cracking of the gels during ageing and drying [8]. Thus, it is important to find a gel structure which can suppress cracking. Gels are prepared by the hydrolysis of an alkoxide and subsequent polymerization in the presence of water. In the preparation of silica gels, it is known that the structure of gels is controlled by the rate of hydrolysis relative to that of polymerization [9, 10]. Few studies, however, have been made on multicomponent systems in order to clarify the effects of process parameters such as the amounts of water and acid on the rates of hydrolysis and polymerization, which determine the structure of gels.

In a previous paper the preparation and crystallization of sol–gel-derived lead titanate was discussed [11]. This paper deals with the effects of the process parameters on the gelation time as well as on the structure of lead titanate gels. The development of gel structure during ageing and drying was analysed with sound waves propagating through gels.

2. Experimental procedure

2.1. Preparation of Pb–Ti complex alkoxide

A Pb–Ti complex alkoxide was prepared by reacting lead acetate and titanium isopropoxide in the presence of methoxyethanol as reported previously [11]. In this process, hydrous lead acetate was dissolved into methoxyethanol, the resulting solution was heated to 130° C to boil off the water contained in the hydrous salt. The solution was cooled to 100° C, then titanium isopropoxide was added slowly. The solution was refluxed at 100° C for 1 h. During refluxing, the reaction between lead acetate and titanium isopropoxide occurred and isopropylacetate (b.p. 85° C) was produced as a by-product. The solution was heated again up to 135° C to distill off the by-product. The complex alkoxide as prepared was called "starting alkoxide solution".

Raman spectroscopy of the distilled by-product liquid suggested that it was isopropylacetate containing a small amount of isopropanol. These compounds could be formed by the following reactions [12, 13]:

$$\mathrm{Ti(OR)_4 + Pb(OCOCH_3)_2}$$

$$\rightarrow \mathrm{PbTiO_2(OR)_2} + \underset{\text{isopropylacetate}}{\mathrm{2CH_3COOR}}$$

$$\mathrm{Ti(OR)_4} + \underset{\text{methoxyethanol}}{x\mathrm{CH_3OCH_2CH_2OH}}$$

$$\rightarrow \mathrm{Ti(OR)}_{4-x}\mathrm{(OCH_2CH_2OCH_3)}x + \underset{\text{isopropanol}}{x\mathrm{ROH}}$$

where $R = -C_3H_7$.

2.2. Preparation, ageing, and drying of gels

Lead titanate gels were prepared by adding an aqueous nitric acid solution of the starting alkoxide solutions of various molarities. The alkoxide molarity, M, was

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TABLE I Typical preparation conditions of gel

Starting alkoxide solution: M = 2.0 [mol l^{-1}]	ME*	Nitric acid solution			M‡	H_2O/Ti	NO_3/Ti
		wt % of HNO_3	d†	Quantity			
6 ml	16.7 ml	15.2	1.08	0.71 ml	0.53	3.0	0.15
6 ml	16.7 ml	20.8	1.11	0.51 ml	0.53	2.0	0.15
6 ml	16.7 ml	40.0	1.25	0.58 ml	0.53	2.0	0.38
6 ml	7.8 ml	40.0	1.25	0.58 ml	0.87	2.0	0.38
6 ml	16.7 ml	50.0	1.30	0.67 ml	0.53	2.0	0.57

*Methoxyethanol.
†Density of nitric acid solution; [g cm^{-3}].
‡Molarity of alkoxide solution; [mol l^{-1}].

defined as the equivalent number of moles of $PbTiO_3$ dissolved in a unit volume of the solution. Various amounts of methoxyethanol were mixed with the starting alkoxide solution in order to adjust the alkoxide molarity. The solution was cooled down to 0° C, and then an aqueous nitric acid solution was added into the alkoxide solution while stirring.

The amount of water and nitric acid added were defined as the number of moles added to one mole of titanium which was dissolved in the alkoxide solution, i.e. [H_2O/Ti] and [NO_3/Ti], respectively. The [H_2O/Ti] and [NO_3/Ti] were controlled by changing both the amount and acidity of nitric acid solution. Typical preparation conditions of gels are shown in Table I.

After the complete addition of nitric acid solution, the solution was poured into cylindrical glass containers and held at 0° C until gelation occurred. The gelation time was defined as that at which the solution became immobilized after the final addition of nitric acid. A cap on the glass containers was fixed tightly to prevent solvent vaporization. Hereafter, the gel so obtained is called "fresh-gel".

The fresh-gel was heated at 70° C and aged for 7 days. During the ageing process, the gels shrunk, with volume of solvent separating out being equivalent to the loss of gel volume. Thus, the shrinkage of gels was defined as

Gel-shrinkage = V_1/V_0 [vol %]
V_1: volume of solvent which was poured out
V_0: initial volume of fresh-gel

(A cap on the container was fixed tightly in order to prevent solvent vaporization during ageing). After ageing, the gel was dried for 2 days at 135° C. (The drying temperature was higher than the boiling point of methoxyethanol.) The gels which experienced the ageing and drying are called "aged-" and "dried-gels", respectively.

2.3. Characterization of fresh-, aged- and dried-gels

2.3.1. Density

Bulk density of fresh- and aged-gels was determined from their weight and volume. Bulk and true densities of the dried-gels were measured by the "Archimedes' method" (light oil with the density of 0.90 [g cm^{-3}] was used) and using a He-pycnometer, respectively.

2.3.2. Elastic modulus

The elastic moduli of fresh-, aged- and dried-gels were determined from the sound-wave velocity propagating through the gels from one face to the other [14]. Piezoelectric transducers were used to generate and detect the sound waves. The travel-time of the longitudinal wave was determined with an oscilloscope. The longitudinal modulus, L, was determined from the bulk density, D_{bulk}, and longitudinal wave velocity, V_l

$$L = D_{\text{bulk}} V_l^2 \qquad (1)$$

3. Results and discussion

3.1. Gelation time

The gelation time was found to be a function of the amount of water as well as alkoxide molarity. Fig. 1 shows the effect of the amount of water, [H_2O/Ti], on the gelation time. When the amount of acid, [NO_3/Ti], was fixed, increasing the amount of water reduced the gelation time. In the range of [H_2O/Ti] from 2.0 to 4.0 the relation between the gelation time, t_g, and [H_2O/Ti] could be expressed as:

$$t_g = A[H_2O/Ti]^{-9.2} \qquad (2)$$

where A is a constant. Greater additions of water resulted in a gelation time longer than expected from

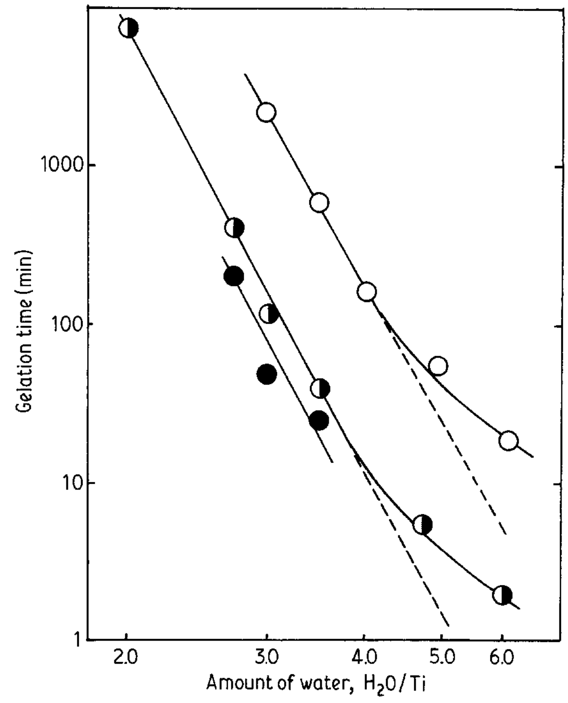


Figure 1 Effect of amount of water on gelation time. M = 0.53 mol l^{-1}, (○) NO_3/Ti = 0.30, (●) NO_3/Ti = 0.08, (◐) NO_3/Ti = 0.15.

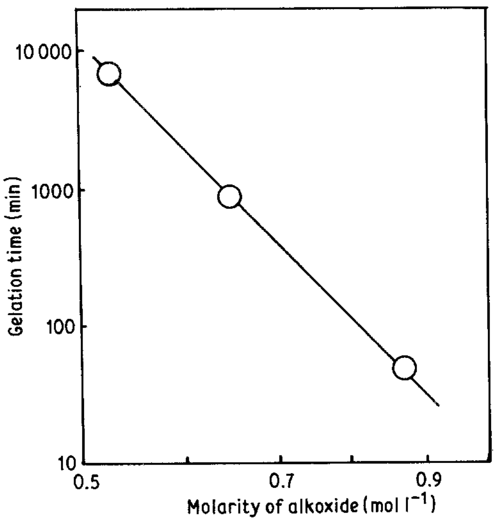


Figure 2 Effect of alkoxide molarity on gelation time. $H_2O/Ti = 2.0$, $NO_3/Ti = 0.15$.

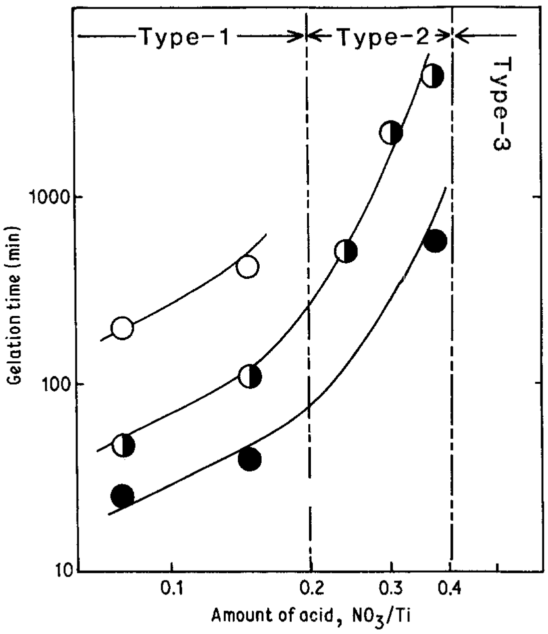


Figure 3 Effects of amount of acid on gelation time and on the appearance of the gel obtained. Type-1, type-2, and type-3 gels correspond to transparent, opaque, and powder-like gels, respectively. $M = 0.53\,mol\,l^{-1}$, (○) $H_2O/Ti = 2.7$, (●) $H_2O/Ti = 3.5$, (◐) $H_2O/Ti = 3.0$.

Equation 2. Dilution of the alkoxide solution with a large amount of water might be responsible for this deviation.

Fig. 2 shows the effect of alkoxide molarity, M, on the gelation time. The gelation time decreased with increasing alkoxide molarity. The relationship between observed gelation time and molarity could be expressed as:

$$t_g = A'M^{-10.1} \quad (3)$$

where A' is a constant.

Hartel *et al.* have studied the precipitation kinetics of the hydrolysis reaction of titanium isopropoxide [15]. They found that the induction time from precipitation depended on both $[H_2O/Ti]$ and M. In our experiment, the gelation time depended on both $[H_2O/Ti]$ and M also. At the gelation time, the viscosity of the alkoxide solution increased rapidly. Since development of a polymer network increases viscosity of the solution, it is thought that the observed gelation time corresponds to the time at which polymers with a critical size capable of further growth were developed. In other words, increases in either the amount of water or alkoxide molarity accelerated the polymerization reaction, causing rapid gelation.

Fig. 3 illustrates the effect of amount of acid on the gelation time. For a fixed amount of water and constant alkoxide molarity, the gelation time increased with increasing amount of acid, indicating that acid suppresses polymerization reaction.

3.2. Gel appearance

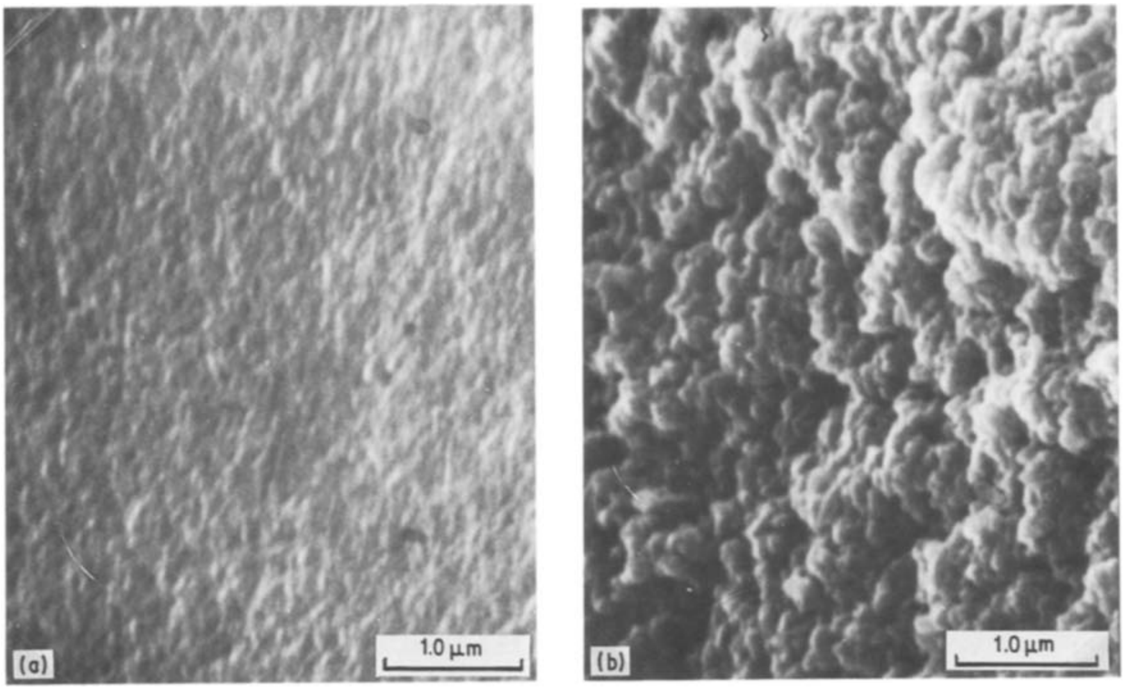
The amount of acid also affected the appearance of the fresh-gels obtained as also shown in Fig. 3. Gels obtained by adding a small amount of acid ($[NO_3/Ti] < 0.20$) were transparent. Gels obtained with a greater amount of acid ($0.2 < [NO_3/Ti] < 0.4$) were opaque. Addition of an excessive amount of acid ($[NO_3/Ti > 0.40$), however, prevented gelation on a large scale, yielding a powder-like gel. The transparent, opaque and powder-like gels will be called type-1, type-2, and type-3 gels respectively in this paper.

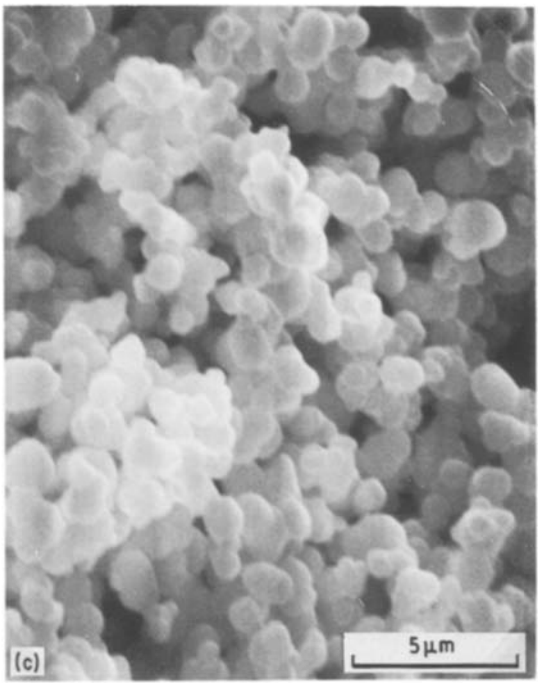
The appearance of the gels reflected their microstructure. The fracture surface of the dried-gels derived from type-1, type-2 and type-3 gels were observed with an SEM and are shown in Fig. 4. (The microstructures of the fresh-gels, however, were not observable because of the solvent present.) No distinctive particles or clusters were observed in the dried-gel for a type-1 gel, indicating that the gel consisted of a polymer-network spread out homogeneously on a large scale. The dried-gel from a type-2 gel consisted of irregularly shaped clusters of 0.5–1.0 μm in diameter, each cluster was connected tightly. Structural fluctuation in these gels caused light scattering, making them opaque. The powder-like gel (type-3) consisted of dense spherical particles about 1.0 μm in diameter, with each particle piled up loosely. It thus appears that acid retards the polymerization reaction, suppressing rapid gelation, and also preventing the formation of a polymer-network. Thus, with increasing amounts of acid, fresh-gels changed from transparent to opaque to powder-like.

Fig. 5 shows the effects of the process parameters $[H_2O/Ti]$, $[NO_3/Ti]$, and M on the appearance of the fresh-gel. The appearance was dependent only upon the amount of acid, not on the alkoxide molarity nor the amount of water. Since the bulk density of fresh-gels increased with increasing alkoxide molarity, due to reduced solvent content in the fresh-gel (see Table II), five kinds of fresh-gels having different characteristics could be prepared: type-1 gels having low and high densities, type-2 gels having low and high densities, and type-3 gels.

3.3. Shrinkage of gels during ageing

When a fresh-gel was aged at 70° C, the gel shrunk while separating the same volume of solvent as the gel-shrinkage. The rate of shrinkage depended upon the preparation conditions. Fig. 6 shows the time-





dependence of shrinkage in type-1 gels. The rate of shrinkage increased with increasing amount of water and also with increasing alkoxide molarity as shown in Figs 6a and b, respectively. It is known that development of a polymer network in gels causes shrinkage during ageing [15]. Thus, extensive polymerization, associated with a large amount of water or high alkoxide molarities, is believed responsible for the rapid shrinkage. The rapid shrinkage of type-1 gels caused cracking even in the ageing process.

The effect of the amount of acid, or essentially that of gel-structure (type-1 versus type-2) on shrinkage was also examined. The results are shown in Fig. 7. (Note that the amounts of water and alkoxide molarity were fixed.) The shrinkage rate increased with increasing amount of acid. Namely, type-2 gels shrunk more rapidly than type-1 gels. Cracking in type-2 gel did not occur in spite of the rapid shrinkage.

Figure 4 SEM photomicrographs of the fracture surface of dried-gels from (a) type-1, (b) type-2, (c) type-3 gels.

As described above, the shrinkage behaviour of type-2 gels was different from that of type-1 gels. In order to understand the origin of the difference, the bulk density and elastic (longitudinal) modulus of aged-gels were measured and the structure development of the gel was studied in a manner similar to that of Walter [17]. The bulk density of aged-gels increased with increasing ageing time due to the gel-shrinkage. Fig. 8 shows the relation between bulk density and elastic modulus where a low-density type-1 gel and a

H_2O/Ti	2	3	4	6	8
Type-1	○	△	□	⬡	▽
Type-2	◑	◭	◨	◑	⧩
Type-3	●	▲	■	⬢	▼

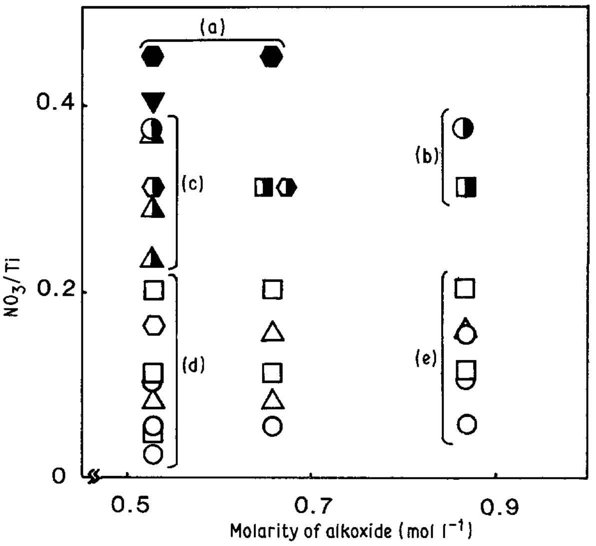


Figure 5 Effects of the amounts of water and acid and of alkoxide molarity on appearance of the gels obtained. (a) Type-3 gel, (b) high density, type-2 gel, (c) low density, type-2 gel, (d) low density, type-1 gel, (e) high density, type-1 gel.

TABLE II Physical properties of dried-gels

Preparation condition			Fresh-gel		Dried-gel						
M*	H_2O/Ti	NO_3/Ti	Gel-type	Bulk-density [g cm^{-3}]	Density			Organic compound [wt %]	L¶	Dielectric constant**	
					Bulk† [g cm^{-3}]	True‡ [g cm^{-3}]	Porosity§ [vol %]			10 kHz	100 kHz
Effect of amount of acid											
0.53	2.0	0.08	1	1.10	3.42	3.87	12	14.0	–	–	–
		0.15	1	1.10	3.46	3.96	13	14.2	–	–	–
		0.38	2	1.11	3.55	4.03	12	14.0	–	–	–
		0.57	3	–	–	4.29	–	17.2	–	–	–
Effect of amount of water											
0.53	2.0	0.15	1	1.10	3.46	3.96	13	14.2	–	–	–
	3.0	0.15	1	1.09	3.53	4.04	13	14.0	–	–	–
Effect of molarity of alkoxide											
0.53	2.0	0.15	1	1.10	3.46	3.96	13	14.2	–	–	–
0.66			1	1.18	3.31	–	–	–	–	–	–
0.87			1	1.22	3.21	4.07	21	–	–	–	–
0.53	2.0	0.38	2	1.11	3.55	4.03	12	14.0	15.1	25.2	15.3
0.87			2	1.20	3.21	4.08	22	13.6	12.4	19.3	14.8

*Molarity of alkoxide [mol l^{-1}].

†Measured by "Archimedes' method".

‡Measured by using He-pycnometer.

§[1-(bulk density/true density)].

¶Longitudinal modulus [GPa].

**Measured at 24° C in 32% of relative humidity.

high-density type-2 gel were aged. The elastic modulus of a low-density type-2 gel ([H_2O/Ti] = 2.0, [NO_3/Ti] = 0.38, M = 0.53 mol l^{-1}) could not be measured because the gel was too weak. The elastic modulus of both type-1 and type-2 gels increased with increasing bulk density during ageing. Comparison of type-2 with type-1 gels at a fixed bulk density showed that elastic modulus of the former was lower than that of the latter, indicating that type-2 gels were softer than type-1 gels. The softness of type-2 gels allows for easy motion of the gels during shrinkage and also relaxation of the stress produced by gel-shrinkage. This, we believe, is why type-2 gels did not crack despite the rapid shrinkage. In summary, gels with low elasticity suppress cracking during ageing.

3.4. Characteristics of dried-gels

Fig. 9 shows the appearance of fresh- and dried-gels. Irrespective of the amount of water and alkoxide molarity, severe cracking occurred when type-1 gels were dried (see Fig. 9, a and a′). For type-2 gels, on the other hand, cracking did not occur and monolithic dried-gels were obtained (see Fig. 9, b and b′, d and d′). The volume of the dried-gel from a high-density type-2 gel was larger than that from a low-density type-2 gel because of the reduced content of solvent in the fresh-gel. For type-3 gels, colloidal particles were located on the bottom of the glass container after drying.

The physical properties of dried-gels are summarized in Table II. When the amounts of water and alkoxide molarity were fixed, both the bulk and true densities of dried-gels increased with increasing amount of acid. Thus, the porosity of the dried-gels remained essentially unchanged. The porosity of dried-gels was less sensitive to the amount of water. The alkoxide molarity, on the other hand, affected the porosity. Increasing alkoxide molarity decreased the bulk density and increased the true density of dried-gels, resulting in increased porosity. The elastic modulus of dried-gels decreased with increasing alkoxide molarity due to the increased porosity (see

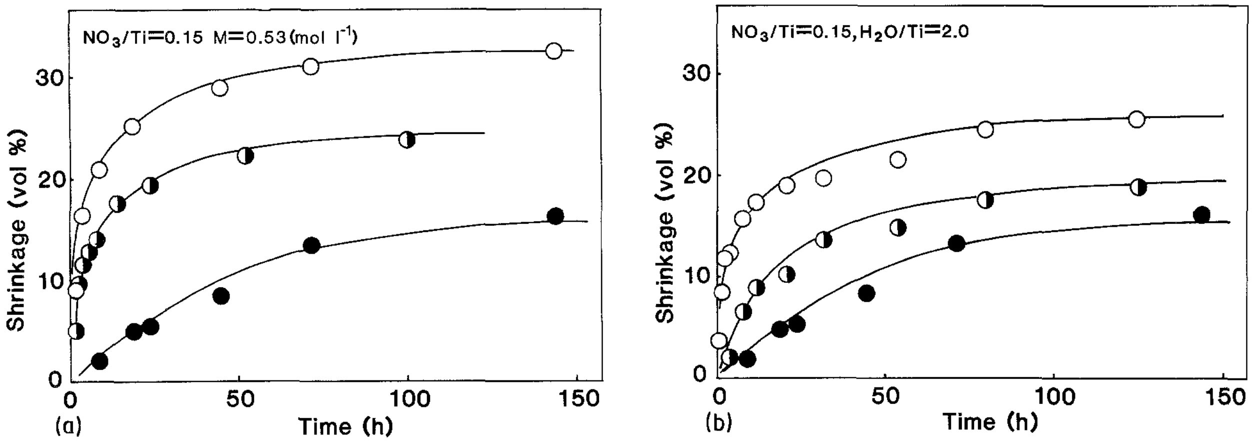


Figure 6 Effects of (a) amount of water ((○) H_2O/Ti = 3.0, (◐) H_2O/Ti = 2.7, (●) H_2O/Ti = 2.0) and (b) alkoxide molarity ((○) M = 0.87 mol l^{-1}, high density gel, (◐) M = 0.66 mol l^{-1}, (●) M = 0.53 mol l^{-1}, low density gel) on gel-shrinkage during ageing at 70° C.

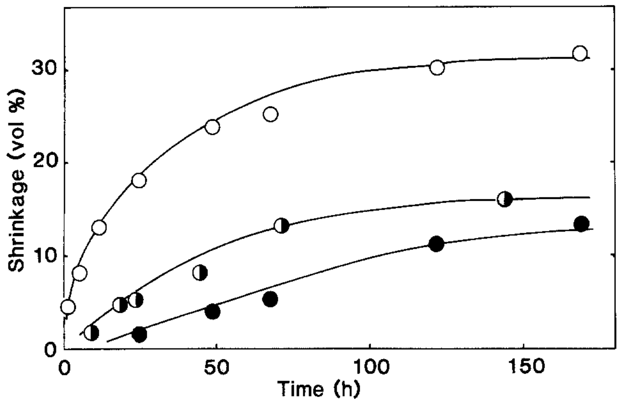


Figure 7 Effect of amount of acid on gel-shrinkage during ageing at 70° C. $H_2O/Ti = 2.0$, $M = 0.53$ ($mol\,l^{-1}$), (○) $NO_3/Ti = 0.38$ (type-2), (◐) $NO_3/Ti = 0.15$ (type-1), (●) $NO_3/Ti = 0.08$ (type-1).

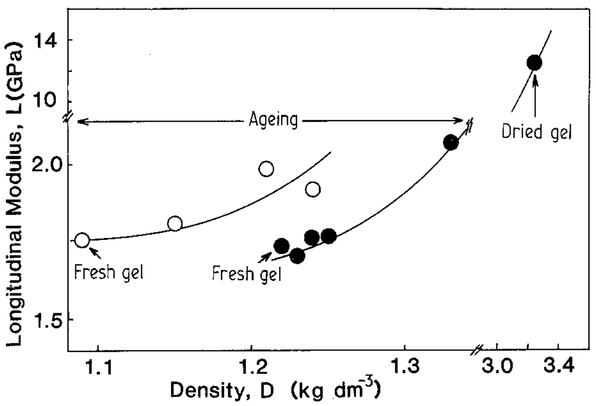


Figure 8 Relation between bulk-density and elastic (longitudinal) modulus of the aged-gels. $L = DV_l^2$, V_l = sound wave velocity, L = longitudinal modulus, D = density. (○) Low-density type-1 gel: $[H_2O/Ti] = 2.0$, $[NO_3/Ti] = 0.15$, $M = 0.53$ $[mol\,l^{-1}]$; (●) High-density type-2 gel: $[H_2O]/Ti = 2.0$, $[NO_3/Ti] = 0.38$ and $M = 0.87$ $[mol\,l^{-1}]$.

Fig. 8 also). The difference in porosity also affected dielectric constants of monolithic dried-gels from type-2 gels.

Dried-gels were X-ray amorphous and contained organic compounds irrespective of the preparation conditions of the fresh-gels. When dried-gels were heated, the organic compounds decomposed at temperatures from 200° to 350° C and crystallization of the $PbTiO_3$ phase occurred at about 480° [18]. The weight loss during heating from 200° to 350° C was about 14.0 wt % except for the powder-like gels. Dried-gels from type-3 gels indicated a high weight loss during heating. Since the powder-like gels were prepared with an excessive amount of acid, removal of the incorporated NO_3-groups in the particles could cause such a large weight loss.

In summary, process parameters such as amount of water and acid and alkoxide molarity critically affect the structure and nature of resultant lead titanate gels; an increasing amount of acid suppresses the development of polymer network and reduces the elastic modulus of resultant gels ("opaque gel"). Gels having a low elastic modulus are desirable for suppression of cracking during ageing and drying.

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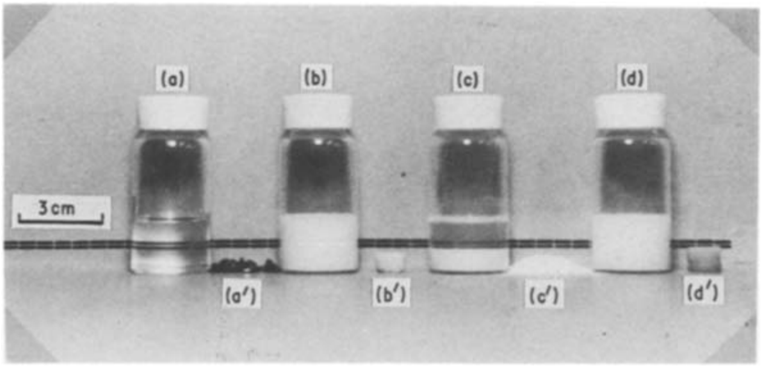

Figure 9 Appearance of fresh-gels and of dried-gels. Fresh-gel: (a) low-density of type-1 gel ($[H_2O/Ti] = 2.0$, $[NO_3/Ti] = 0.15$, $M = 0.453$ $[mol\,l^{-1}]$), (b) low-density type-2 gel ($[H_2O/Ti] = 2.0$, $[NO_3/Ti] = 0.38$, $M = 0.38$ $[mol\,l^{-1}]$), (c) type-3 gel ($[H_2O/Ti] = 2.0$, $[NO_3/Ti] = 0.57$, $M = 0.53$ $[mol\,l^{-1}]$), (d) high-density type-2 gel ($[H_2O/Ti] = 2.0$, $[NO_3/Ti] = 0.38$, $M = 0.87$ $[mol\,l^{-1}]$). Dried-gels of (a')–(d') were derived from fresh-gels (a)–(d), respectively.