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Sol–gel-derived $PbTiO_3$

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The sol–gel process is a technique which is applicable for forming ceramic materials. In this process, liquid precursor materials are reacted to form a sol which then polymerizes into an inorganic polymeric gel. Advantages of this process over standard powder preparation of ceramics are: purity, homogeneity, control of macro- and micro-structures, and low processing temperatures. In our laboratory the sol–gel process has been used to form lead titanate. We detail a procedure which has produced dried monolithic gels up to 1.5 cm in diameter. The as-dried gels have not been exposed to temperatures above 40° C and are X-ray amorphous. Samples of the gels were crushed into powder and heated at 8° C min^{-1} to various temperatures up to 500° C, held for a variety of times, and then cooled to room temperature. After certain annealing procedures crystalline phases were observed. The initial crystalline phase to emerge has not yet been identified. Upon further annealing this phase transforms to tetragonal $PbTiO_3$.

1. Introduction

The work presented here stems from an effort to develop a technique for preparing monolithic titanate ceramics by a sol–gel process and to investigate the properties of the resulting materials. Lead titanate has been the focus of the current study. Although pure lead titanate has not proved to be a technologically important material when prepared by conventional processing procedures, it is an interesting material with potentially useful piezoelectric properties [1].

The sol–gel process has been used to produce a wide variety of polycrystalline and amorphous materials at significantly lower temperature than traditional ceramic or glass fabrication methods [2, 3]. The process is basically a wet chemical technique consisting of the following steps:

1. Preparation of the appropriate metal alkoxide solution.
2. Hydrolysis.
3. Polymerization.
4. Drying.
5. Firing.

Due to the liquid nature of the constituents and the diversity of the processing variables possible, sol–gel processing can offer many advantages in producing ceramics [4]. They are

(a) purity;
(b) homogeneity;
(c) easy to form in a variety of structures (macro- and micro-);
(d) low-temperature processing; and
(e) unique combination of properties.

Sol–gel processing has been gaining interest in the area of synthesizing ceramic materials [2, 3]. One area of particular interest is electronic ceramics. Here the merits of sol–gel processing, such as high purity, molecular homogeneity, and lower processing temperatures, can offer significant advantages over conventional processing methods. The sol–gel process has been used to produce a wide variety of ceramic materials in powder or monolithic form.

Multicomponent oxide gels can be processed in a manner similar to single-component oxide gels [5]. A multicomponent or complex alkoxide

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can be prepared by reacting a combination of single alkoxides, or through the addition of soluble inorganic salts to single or complex alkoxides. The reaction of a partially hydrolysed alkoxide of species M with the alkoxide of species M′ occurs to form a double alkoxide and an alcohol. Alternatively, the species from an inorganic salt can be incorporated into multicomponent alkoxides as well as into the alkoxide sol structure itself. In this work, the precursor used to form lead titanate gels was prepared through the reaction of a lead salt (lead acetate) with titanium alkoxide (titanium isopropoxide).

2. Experimental procedures

2.1. Synthesis of complex alkoxide

As described earlier [6] we prepared a complex alkoxide by reacting lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, with titanium isopropoxide, $Ti(OC_3H_7)_4$, in the following manner: lead acetate was dissolved in methoxyethanol ($C_3H_8O_2$) in a 1:4 molar ratio at 70° C in a three-neck reaction flask. When the lead acetate had dissolved, the reaction flask was fitted with a reflux condenser and the solution was heated to approximately 118° C to begin removing the adsorbed water. As the water was removed, the temperature of the vapours reaching the top of the reflux condenser increased from 100° C to 124° C (the boiling point of methoxyethanol), indicating the removal of water. The solution was then cooled to 100° C and titanium isopropoxide was added to the lead acetate to yield a 1:1 molar ratio of lead to titanium. As the lead acetate and titanium isopropoxide reacted, isopropyl acetate was produced and volatilized from the solution. As the isopropyl acetate was removed, the temperature of the vapours reaching the top of the reflux condenser increased from 85° C (the boiling point of isopropyl acetate) to 124° C. The resulting solution was a gold-coloured liquid with a density of approximately 1.5 to 1.6 g cm^{-3} and a viscosity of approximately 10 cp (10^{-2} N sec m^{-2}). Further heating of the solution to remove additional solvent resulted in an amber-brown liquid with a density of ~1.8 g cm^{-3} and a viscosity ranging from 45 to 98 cp (0.045 to 0.098 N sec m^{-2}).

2.2. Gel preparation

Gels of the complex alkoxide were prepared by combining the complex alkoxide with varying amounts of solvent (methoxyethanol). The water for hydrolysis was then introduced as a solution of methoxyethanol, water and nitric acid. The solutions were mixed together at room temperature and then poured into polystyrene petri dishes. The amount of water added was based upon the amount of titanium isopropoxide used to prepare the complex (4 mol H_2O : 1 mol alkoxide). 2 mol water are sufficient to bring about gelation. The optimum amount of water necessary for the formation of monoliths will be the focus of further study.

Previously [6] we had reported a limit of 0.004 mol HNO_3 : 1 mol H_2O as the concentration of HNO_3 above which a precipitate would form. This limit is process-sensitive and up to 0.08 mol of HNO_3 : 1 mol H_2O have been used without the formation of precipitates.

2.3. Drying and firing

Gels derived from the complex were allowed to dry at room temperature. Drying was nearly complete in three to four weeks.

Pieces of the gels were fired in air in the following manner. The initial heating rate was 3° C min^{-1} to 400° C with 1 h holds at 200 and 400° C to allow for the removal of water and organics. From 400° C, the temperature was increased at a rate of 8° C min^{-1} to 600° C with a 1 h hold at 600° C.

Samples of the dried gel were also crushed to a powder and annealed for a series of times and temperatures using a constant heating rate of 8° C min^{-1} in each case [7]. The annealed powders were examined at room temperature using X-ray diffraction.

3. Results and discussion

The gels prepared from the complex remained transparent after drying as shown in Fig. 1. The bulk density of the dried gels is approximately 3 g cm^{-2}. As mentioned earlier, the gels shrank approximately 70 to 80% during drying and cracking of the samples did occur. A number of samples dried to their final dimensions without cracking but developed cracks a short time after. This may be attributed to stresses developed during the large shrinkages. Pieces up to 1.5 cm in diameter have been obtained from the cracked gels. These samples tend to maintain their integrity until removed from the petri dishes. Cracking may have resulted from the action of

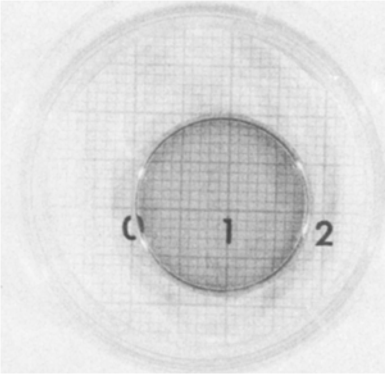

Figure 1 As-dried lead titanate gel. Initially the sol filled the petri dish. Gelation occurred at room temperature and the gel shrank. The markers are 1 cm apart. The gel is estimated to be 50% porous.

moisture in the atmosphere which may act chemically and/or physically in combination with residual stresses to bring about cracking.

The dried gels are amorphous by X-ray diffraction as shown in Fig. 2. The diffraction pattern of the gels fired to 600° C and then cooled to room temperature is shown in Fig. 3 and corresponds to the pattern of tetragonal $PbTiO_3$. A series of anneals for various times and temperatures revealed the presence of a metastable intermediate phase appearing in the transformation of the amorphous gel to the tetragonal $PbTiO_3$ [7]. This metastable phase has not been attributed to the component oxides or any known organic derivative of these elements, nor has it been attributed to any known derivative of $PbTiO_3$. Fig. 4 is a time–temperature phase diagram showing the phase (amorphous, unknown, tetragonal) observed for the appropriate hold time at the appropriate temperature. It should be pointed out that in all cases a heating rate of $8° \mathrm{C\,min^{-1}}$ was used up to the annealing temperature, then the temperature was held. As shown in Fig. 4, at the lower temperatures the amorphous phase was observed. The unknown phase was observed at temperatures as low as 400° C (after annealing for 6 h). As the annealing time was increased, a mixture of tetragonal $PbTiO_3$ and the unknown phase was observed. As the annealing temperature was increased, the tetragonal phase appeared after shorter annealing times. For those anneals with no hold-time at temperature, tetragonal $PbTiO_3$ was not observed until 470° C.

Differential thermal analysis (DTA) was run on a sample which was heated at the same constant rate of $8° \mathrm{C\,min^{-1}}$ as the anneals. The crystallization temperature was observed to be about 480° C as evidenced by the sharp exotherm in the DTA results [7]. This is in agreement with Takashige *et al.* [8], who found T_{crys} for samples prepared by a melt-quench technique to occur between 450 and 600° C. They also reported that, after crystallization, the ferroelectric anomaly in the DTA curve at 490° C did not appear until the melt-quench samples were heated to 900° C. Our gel-derived materials did not exhibit the ferroelectric anomaly in the DTA curve until heating to 550° C. This result seems to indicate that, although crystalline $PbTiO_3$ is observed by

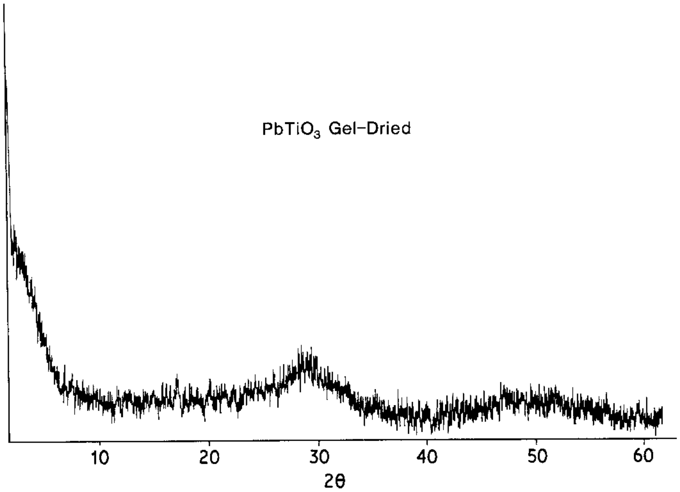

Figure 2 X-ray diffraction spectrum for an as-dried lead titanate gel. The gel is X-ray amorphous.

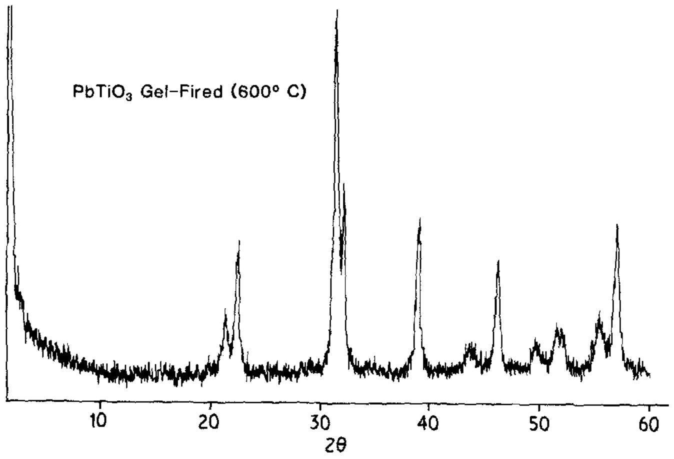

Figure 3 X-ray diffraction spectrum for a lead titanate gel heated to 600° C for 1 h. The spectrum corresponds to tetragonal PbTiO$_3$.

X-ray diffraction below 550° C, the degree of crystallinity or the perfection of the crystalline state is such that the phase transformation at 490° C is not significant.

4. Summary

Amorphous lead titanate has been prepared by a sol–gel method. The crystallization temperature at a constant heating rate of 8° C min^{-1} was observed to be 470° C, which is in agreement with values reported in the literature for the crystallization of amorphous lead titanate prepared by other methods. Our amorphous material will crystallize at temperatures as low as 400° C with sufficient annealing time. The absence of the ferroelectric anomaly prior to

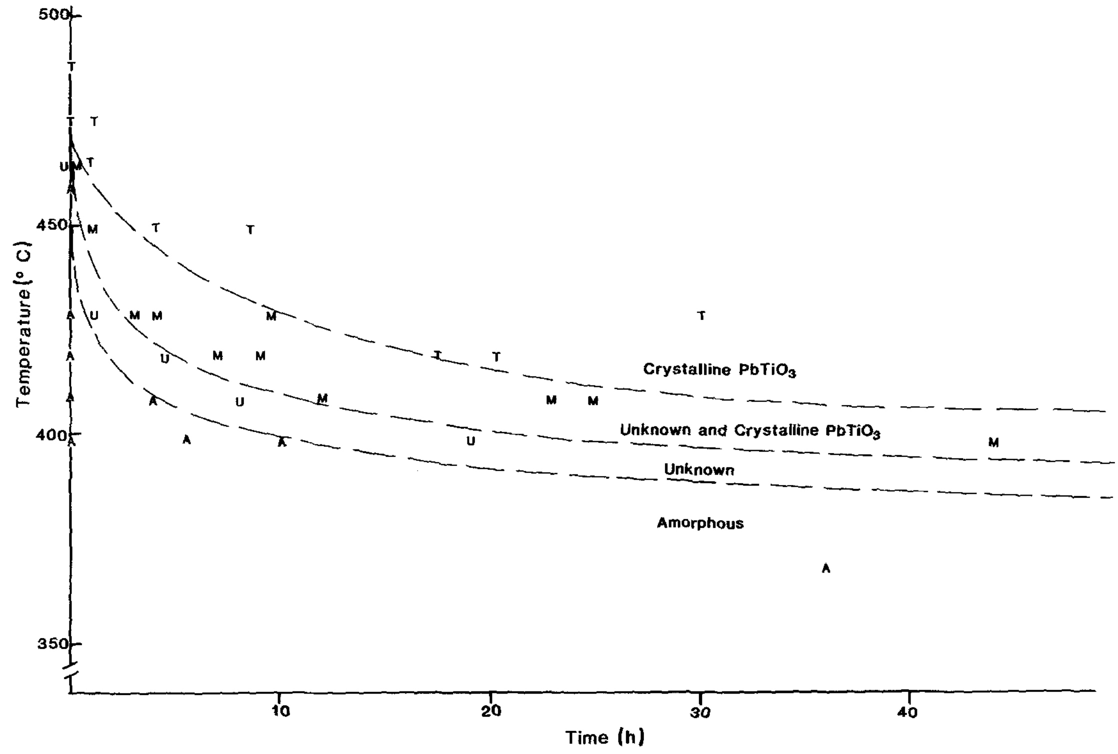

Figure 4 Time–temperature phase field for annealing of dried lead titanate gels. A heating rate of 8° C min^{-1} up to the hold temperature was used in all cases. The phase(s) observed by X-ray diffraction are indicated as follows: (T) crystalline PbTiO$_3$ (tetragonal); (M) unknown and crystalline PbTiO$_3$; (U) unknown; (A) amorphous.

annealing above 550° C may be the result of a low degree of crystallinity or crystal perfection.

Acknowledgement

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References

1. B. JAFFE, W. R. COOK and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, New York, 1971) p. 115.
2. C. J. BRINKER, D. E. CLARK and D. R. ULRICH (editors), "Better Ceramics Through Chemistry" (North-Holland, New York, 1984).
3. L. L. HENCH and D. R. ULRICH (editors), "Ultrastructure Processing of Ceramics, Glasses and Composites" (Wiley–Interscience, New York, 1984).
4. J. B. BLUM, Proceedings of 34th Electronic Components Conference (IEEE, New York, 1984) p. 407.
5. B. E. YOLDAS, *J. Mater. Sci.* **14** (1979) 1843.
6. S. R. GURKOVICH and J. B. BLUM, "Ultrastructure Processing of Ceramics, Glasses and Composites", edited by L. L. Hench and D. R. Ulrich (Wiley–Interscience, New York, 1984) p. 152.
7. *Idem, Ferroelectrics* **62** (1985) 189.
8. M. TAKASHIGE, T. NAKAMURA, H. OZAWA, R. UNO, N. TSUYA and K. I. IRAI, *Jpn. J. Appl. Phys.* **19** (1980) L255.

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