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Preparation of PLZT powders from several aqueous solutions

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Fine, soft agglomerate and chemically homogeneous PLZT powders were prepared from nitrate, chloride and alkoxide precursors. The preparation is based on a coprecipitation method in which the aqueous clear solution of multicomponent systems is reacted with ammonia gas at the liquid surface. As-dried powder characteristics – the microstructure of agglomerates, colour and X-ray diffraction structure – were similar in all cases; however, the properties of calcined powders and of "two-stage" sintered pellet were affected not only by precursors, but also by postprecipitation processing: (a) washing with organic solvent, (b) drying and ageing, (c) calcining. A novel lattice behaviour, i.e. decomposition and recovery of perovskite structure of calcined powders regardless of precursors, was found over a wide temperature range from room temperature to 1150° C. Transparent ceramics were fabricated by sintering the acetone washed-aged powder derived from $TiO(NO_3)_2$ precursor.

1. Introduction

Ferroelectric ceramics of lanthanum-modified lead zirconate titanate (PLZT) have various electro-optic properties which vary with chemical compositions [1]. Many studies have been made of the fabrication and properties of ceramics prepared from mixed oxide raw powder (MO) as reported in the literature [2]. Recently, instead of MO raw powder, which often leads to compositional and structural inhomogeneities in ceramics, a chemical preparation method (CP) has been developed, i.e. hydration of alkoxides [3], and coprecipitation of oxyhydroxides [4, 5], oxalates [6] and citrates [7]. Powder processing has also been investigated; i.e. high humidity [8], spray drying [4] and freeze drying [9]. However, almost all PLZT ceramics have been sintered by hot-pressing, which is unsuitable for mass-production processing. In any case, these methods which use alkoxide precursors or hot-pressing, are too expensive.

In the present paper, to fabricate low-cost, high-quality PLZT ceramics, preparation from inorganic salts and sintering techniques without hot-pressing are investigated.

2. Experimental procedure

2.1. Powder preparation

As common starting reagents, lead nitrate $Pb(NO_3)_2$, oxyzirconium nitrate $ZrO(NO_3)_2 \cdot 2H_2O$ and lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ were used. For titanium, titanium tetrachloride $TiCl_4$, titanium nitrate $TiO(NO_3)_2$ and titanium iso-propoxide were chosen. The titanium nitrate solution was prepared by reacting titanium tetrachloride with ammonia solution to form a precipitate. The precipitate was washed free of chlorides and dissolved in nitric acid. Titanium contents in the titanyl solution were determined by gravimetric analysis.

The mixed solution of composition $Pb_{0.92}La_{0.08}(Zr_{0.65}Ti_{0.35})_{0.98}O_3$ (PLZT 8/65/35) was prepared, and an added 10 wt % excess of PbO as lead nitrate was dissolved in the solution to increase the densification of ceramics during the early stages of sintering. A small amount of hydrogen peroxide was also added to the solution according to the procedure described by Murata *et al.* [10].

Fig. 1. shows the flow diagram of preparation from $TiCl_4$ precursor. To avoid the formation of $PbCl_2$, a two-step precipitation method was used: coprecipitating the complex oxyhydroxide gel of titanium, zirconium and lanthanum at about 1°C; with ammonia solution, adding lead nitrate solution to the solution which was controlled at about pH 9.4, and the temperature kept at about 40° C; filtering and washing with water until no reaction for Cl^- ion with $AgNO_3$ was observed; rinsing with acetone; drying at 40° C overnight.

Fig. 2 shows the flow diagram in the case of titanium alkoxide. Titanium alkoxide was added directly to nitric acid and clear titanyl solution was obtained. Then four mixed nitrate solutions were reacted with ammonia gas. In Fig. 3, titanium nitrate solution was used. Four mixed nitrate solutions were also reacted with ammonia gas. The coprecipitates were washed with water, rinsed with acetone or ethanol, dried at 40°C overnight and aged under reduced pressure for longer than a week. Spray drying of the mixed nitrate

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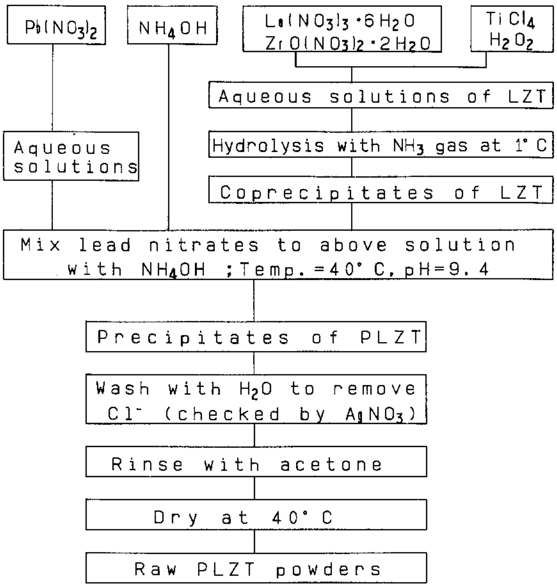

Figure 1 Flow chart for chemical preparation process of PLZT powder from $TiCl_4$ precursor.

solutions was also done. The dried powder was subsequently calcined at 300 to 1000° C for 0.5 to 14 h under O_2 gas flow rates of $0.5\,l\,min^{-1}$ and milled with 2 mm YTZ ball (Nippon Kagaku Togyo Co., Ltd) in a teflon container.

TG-DTA, X-ray diffractomer (XRD) and SEM were used in the characterization of precipitated, dried and calcined powders.

2.2. Ceramic fabrication

Calcined and milled powder was uniaxially cold pressed at $1\,ton\,cm^{-2}$ into a pellet of 1.3 cm diameter and 0.2 cm thick; no binder was used. The pellet was sintered using a two-stage technique [11] at 950 to 1150°C for 1 to 12 h in an oxygen atmosphere without setting sand and atmosphere powder: first, the pellet was sintered in a platinum *schale* for 1 h; subsequently, to remove the excess PbO in the sintered body, it was replaced in an alumina *schale* and resintered for 12 h. Fig. 4 shows the physical arrangement of the two-stage sintering.

Weight loss, density, microstructure and optical transmission of the sintered pellets were examined.

3. Results and discussion

The coprecipitates obtained by hydrolysing the mixed nitrate solutions are all reddish yellow gels, which are amorphous to XRD. When H_2O_2 is not added, white gels are formed which are also amorphous to XRD. According to the preliminary hydrolysis of a lead nitrate solution, the chemical effect of the addition on the precipitates is essentially that precipitated crystalline lead hydroxide is oxidized and converted into a higher state of oxidation. Investigation by XRD, TG, and chemical analysis suggests that a major amorphous phase, $3PbO\cdot 2PbO_2\cdot 3H_2O$ is formed and a small amount of a second amorphous phase – $PbO_2\cdot 2H_2O$ and/or $Pb_2O_3\cdot 3H_2O$ – is also contained. Therefore, the reddish yellow coprecipitate of these multicomponents contains an amorphous higher oxide of lead.

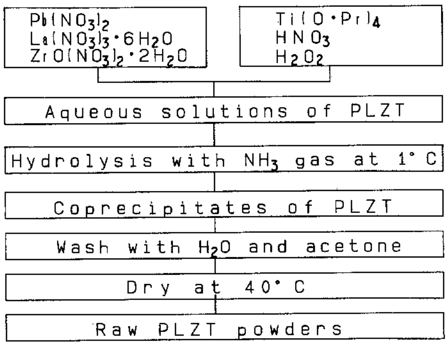

Figure 2 Flow chart from titanium iso-propoxide precursor.

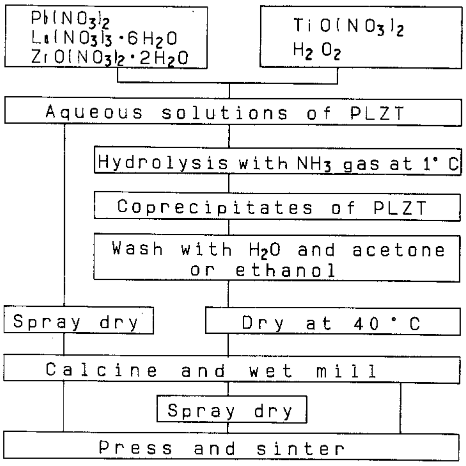

Figure 3 Flow chart from $TiO(NO_3)_2$ precursor.

Postcoprecipitation processing – washing and drying – is also important to produce sinterable powders as well as coprecipitation. After conventional treatments of washing with water and drying in an air oven, hard lumps with a glassy surface were formed. Nonconventional processing – rinsing with organic solvent and drying at low temperature – gives soft agglomerated powders. On the other hand, spray drying gives white powders, which show a single phase of lead nitrate on the XRD pattern. Fig. 5 shows typical scanning electron micrographs for as-precipitated particle and spray-dried powders. The as-precipitated primary particles are about 0.02 μm diameter. A large number of the particles mutually agglomerate to form distinct secondary particles with agglomerate sizes of about 0.1 μm. These secondary particles further weakly bond to each other. The 0.3 to 3 μm agglomerates of the spray-dried powder were spherical, with a broad size range reflecting the distribution of drop sizes obtained from a spray nozzle.

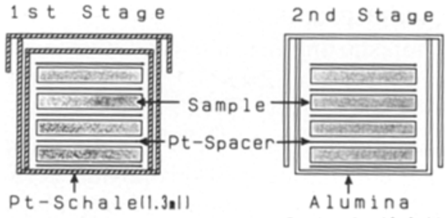

Figure 4 Physical arrangement for two-stage sintering of PLZT ceramics. Samples are sintered at 950 to 1150° C, 1 h for the first stage and 1000 to 1100° C, 12 h for the second stage.

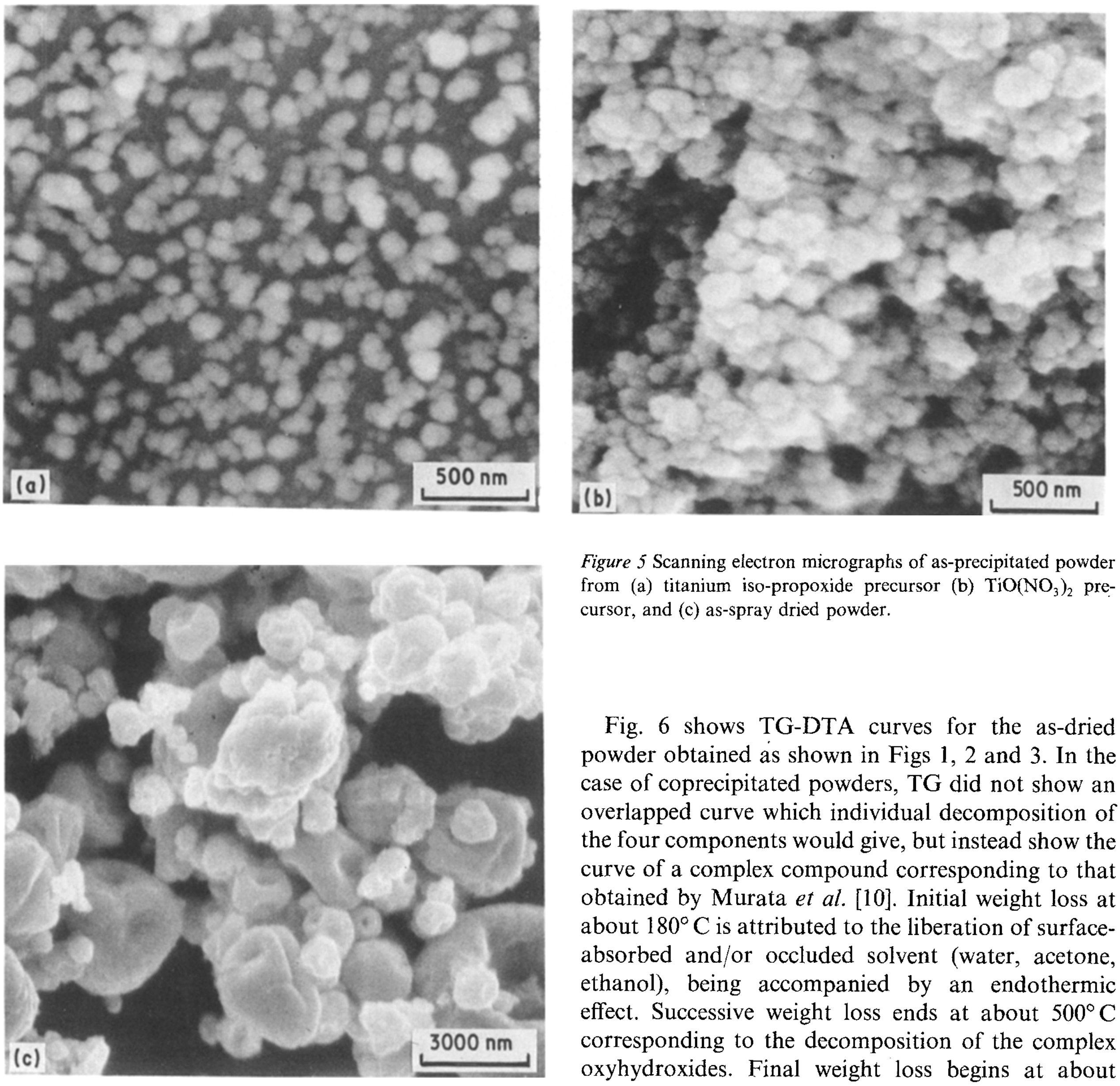

Figure 5 Scanning electron micrographs of as-precipitated powder from (a) titanium iso-propoxide precursor (b) $TiO(NO_3)_2$ precursor, and (c) as-spray dried powder.

Fig. 6 shows TG-DTA curves for the as-dried powder obtained as shown in Figs 1, 2 and 3. In the case of coprecipitated powders, TG did not show an overlapped curve which individual decomposition of the four components would give, but instead show the curve of a complex compound corresponding to that obtained by Murata *et al.* [10]. Initial weight loss at about 180° C is attributed to the liberation of surface-absorbed and/or occluded solvent (water, acetone, ethanol), being accompanied by an endothermic effect. Successive weight loss ends at about 500° C corresponding to the decomposition of the complex oxyhydroxides. Final weight loss begins at about 820° C because of the evaporation of PbO. The broad exotherm around 250 to 300° C probably relates to the change of atomic configuration induced by the liberation of trapped solvents. At about 500° C, an additional exotherm is observed.

The spray-dried powder exhibits a similar weight loss to that of the coprecipitated sample. The amount of weight loss agrees with the calculated loss assuming that lead, lanthanum, zirconium and titanium are all present in the powder as nitrate compounds. DTA shows the endothermic effects at about 430° C due to the decomposition and subsequent melting of lead nitrate, corresponding to that obtained by Thomson [4].

The XRD patterns of calcined powders were observed on calcine processing from room temperature to 1150° C. In the coprecipitated powder, a solid state reaction occurs above 500° C/5 h ($TiCl_4$ and $TiO(NO_3)_2$) or 550°C/2 h (Ti-alkoxide) and the cubic phase of PLZT appears. These diffraction profiles become sharper and higher with increasing the calcination temperature.

The integral diffraction intensity of powders calcined at 550° C is comparable to higher-temperature calcined powders such as 1000° C. Therefore, very fine

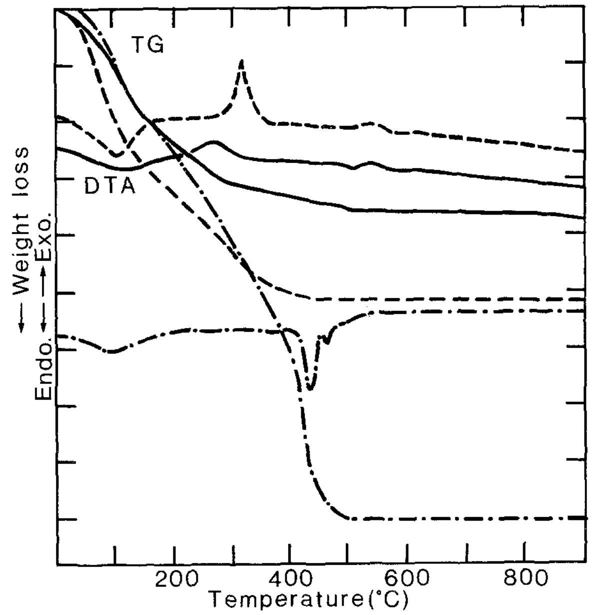

Figure 6 DTA and TG curves of the dried powder, measured at a heating rate of $10° C\,min^{-1}$ in air. (---) $TiCl_4$, (——) $Ti(OPr^i)_4$, (---) $TiO(NO_3)_2$.

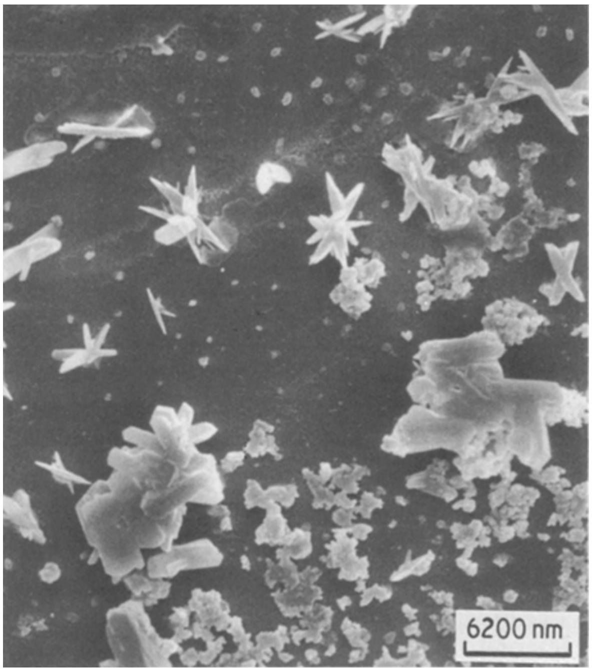

Figure 7 Crystals of $PbCl_2$ grown in calcined (800° C, 2 h) powders from $TiCl_4$ precursor.

PLZT crystallites are formed at the lower temperatures, reflecting the atomic-scale homogeneity in the CP method. However, when as-dried powders prepared from the present coprecipitation methods were calcined, the PLZT lattice, which gradually grew with increasing temperature above 500° C, decomposed at about 900° C and regrew at 1000° C. On the other hand, when aged-dried powders were calcined, the PLZT intensity monotonically increased with increasing temperature and in these lattice decomposition did not occur.

Fig. 7 shows the $PbCl_2$ crystals which grow during calcination and virtually cannot be found by conventional XRD analysis because of their small amount. Probably during coprecipitation, a small amount of insoluble $3PbO \cdot PbCl_2 \cdot nH_2O$ is formed which cannot be detected by Cl^- checking during washing. Good quality ceramics are not sintered from powders containing chloride, because this leaves large voids as the result of vaporization.

The typical difference in reactivity between as-dried powders and aged powders is shown in Fig. 8. The weight loss which was measured by TG heating to 500° C gradually decreased from 19 wt % to 12 wt % over four months when the as-dried powder was aged at room temperature. This means that desorption of a large amount of absorbed solvents and dehydration resulted from oxolation in the particles gradually occur, in spite of dried up feature. The physicochemical changes of the surface and the bulk of the particles are intimately linked with the development of chemical reactivity.

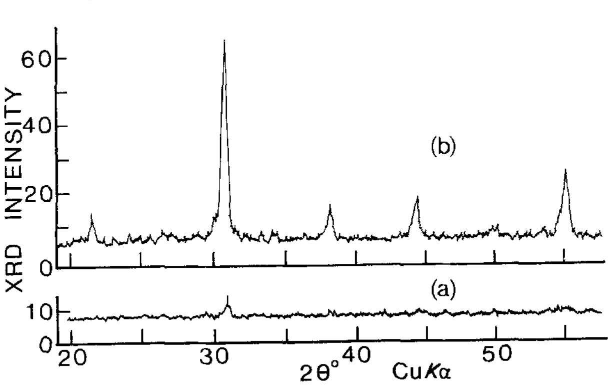

Figure 8 XRD patterns of calcined (a) as-dried and (b) aged powders.

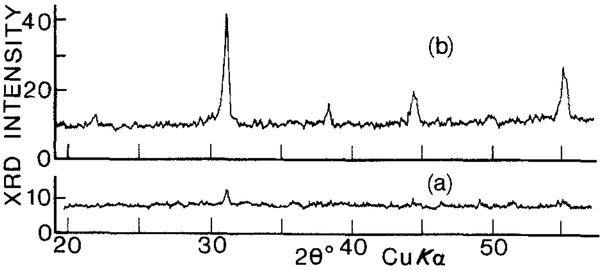

Figure 9 XRD patterns of powders calcined in (a) air and (b) oxygen.

The effect of oxygen atmosphere on the solid state reaction or crystallity is shown in Fig. 9. If atomic-scale homogeneity is achieved in CP powder, the rate limiting mechanism in the overall formation of perovskite structure must be associated with the interdiffusion of cations and the rearrangement of the oxygen lattice within a certain short range, rather than the counterdiffusion of cations through the reaction product layer which is formed on the surface of the reactant oxides. Oxygen gas accelerates the nucleation and growth of PLZT crystallite by supplying lattice oxygen atoms from the gas phase. The oxygen atmosphere also prevents oxides, especially PbO, from decomposing to the metal.

In Fig. 10, dramatic lattice decomposition is seen to occur on reheating to 1150° C/1 h. When this XRD sample is held and aged on an XRD holder at room temperature, perovskite lattice recovery again occurs. These phenomena are also observed in the powder calcined at 700° C/4 h as shown in Fig. 11. These facts indicate that the difference of energy states between these structures is small and that these lattice changes

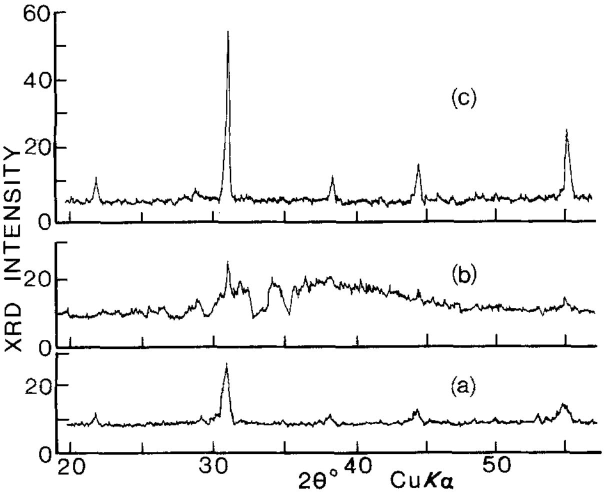

Figure 10 XRD patterns observed during successive heat treatment and ageing for the same powder. After calcining at (a) 800° C, 2 h, (b) after reheating at 1150° C, 1 h, and (c) after 10 days ageing at room temperature.

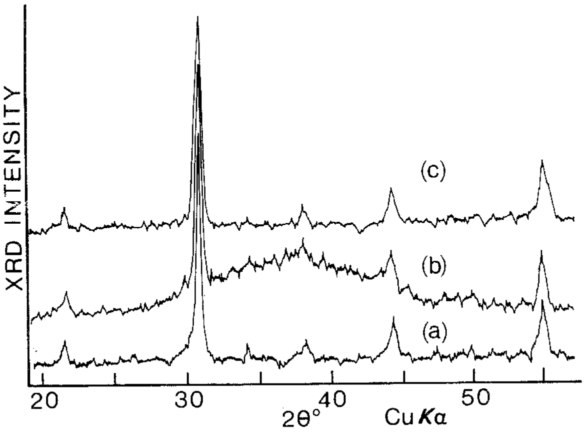

Figure 11 XRD patterns observed for calcined (700° C, 4 h) powder aged at room temperature. (a) 19 h, (b) 44 h, (c) 52 h.

Figure 12 PbO crystals grown on the inside of a sintered (950° C, 1 h) pellet.

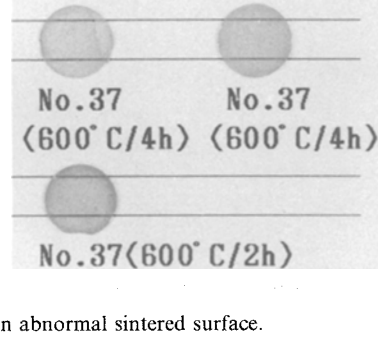

Figure 13 An abnormal sintered surface.

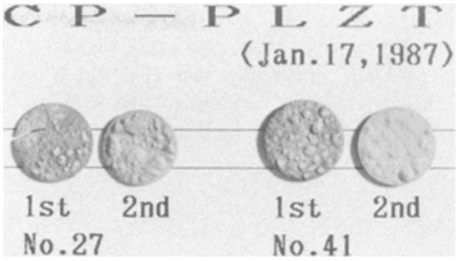

Figure 14 Examples of the two-stage sintered, polished PLZT ceramics.

easily occur even at room temperature. The instability of the perovskite lattice of calcined powders was often observed, regardless of the coprecipitation process.

After the first step of sintering above 800° C, agglomerates of PbO crystal, which are shown in Fig. 12, were found almost inside the pellets. However, when the calcined powder that is coprecipitated from $TiO(NO_3)_2$ precursor, washed with acetone and aged under reduced pressure is sintered, significant agglomeration of PbO is not observed. The surface of pellets containing these agglomerates are pushed up by the pressure of the PbO gas which rapidly evaporates above 1000° C (Fig. 13). Therefore, many voids with a wide size range distribution are observed on the inside of the pellet. Once these phenomena in the first stage of sintering have occurred, it is difficult to eliminate the large voids during the second stage.

Fig. 14 shows transparent ceramics, raw powders of which are prepared from $TiO(NO_3)_2$ precursor, washed with acetone and aged for many days. Work in progress indicates that optimization of the two-stage sintering process is possible to eliminate small pores which remain in the transparent ceramics.

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