Large electromechanical anisotropic modified lead titanate ceramics

Part 1 Processing

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Modified lead titanate (PT) oxalates were prepared by mixing an ethanol solution with (calcium, lanthanum, neodymium, samarium or gadolinium) and titanium with an ethanol solution of oxalic acid containing lead, and (cobalt and tungsten) or manganese by blending. The resulting complex oxalate, after washing with ethanol for several times, was an amorphous powder with a very fine particle size. The amorphous coprecipitate gave, on calcining, a high sinterable modified lead titanate powder of compositions $(Pb_{0.76}Ca_{0.24})$ $((Co_{0.5}W_{0.5})_{0.04}Ti_{0.96})O_3$ or $(Pb_{0.88}La_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ which, on sintering, produced highly densified bodies ($\geqslant 98\%$ theoretical density) at relatively low temperatures (1100 and 1150° C for Ca-PT and Ln-PT, respectively). Linear thermal expansion measurements, microstructural development of the modified lead titanates, and the influence of grain size on c/a ratio have also been studied.

1. Introduction

Lead titanate is a material with a perovskite structure (ABO_3) in which a ferroelectric phase transition occurs at 490° C. Above that temperature its crystal structure is cubic and below the Curie point the cubic phase changes to tetragonal phase. Owing to such a phase change, a cell dimension change is also produced and, consequently, a strong internal stress may be induced. In this way the preparation of pure dense $PbTiO_3$ ceramics of high resistivity becomes very difficult, because $PbTiO_3$ ceramics gradually disintegrate into powder when they are cooled below the cubic-tetragonal phase transition temperature [1, 2]. Attempts have been made to make mechanically strong and densified $PbTiO_3$ ceramic bodies using several dopants. Recently, Gurkovich and Blum [3] and Hayashi and Blum [4] reported the preparation of $PbTiO_3$ from organometallic precursors. Nevertheless, the problem remains of its sintering at sufficiently low temperature to avoid the large thermal expansion anisotropy at the cubic-tetragonal transition at 490° C. For these reasons the sintering of $PbTiO_3$ is achieved using additives, and its commercial application is being developed.

The first major contribution of titanate-related ceramics was reported by McQuarrie [5]; however, there was no emphasis concerning the lead titanate-based ceramics. Subbarao [6] attempted to obtain densified $PbTiO_3$ ceramic bodies by means of the addition of small amounts of niobium or tantalum oxides, and although the sintering was enhanced, no higher than 95% theoretical density was achieved. Tien and Carlson [7] studied the effect of several additives on sintering and properties of $PbTiO_3$, and found that a small addition of CaF_2 produced a dense

$PbTiO_3$ ceramic with a low dielectric constant and an improved piezoelectric coefficient, d_{33}. Ueda and Ikegami [8] studied the influence of several additives on piezoelectric properties of $PbTiO_3$; in particular, $Bi_{2/3}TiO_3$ improved density (97%) and the piezo-electric constants. Recently Japanese researchers [9-12] have investigated the dielectric-piezoelectric $(d-p)$ properties of modified $Ca-PbTiO_3$ and rare earth-$PbTiO_3$ ceramics showing the strong influence of both CaO and rare earth oxides on their dielectric, piezoelectric and mechanical properties.

Although the preparation of modified lead titanate is relatively easy, nevertheless the vapour pressure of lead oxide at the sintering temperature is considerable, by which a rigorous control of the same is necessary in avoiding inhomogeneities in the microstructure of the sintered bodies which could give rise to the appearance of bimodal grain size, microcracking, lower density, and lower piezoelectric constants. In order to achieve a better control of the microstructure of sintered bodies, the present work deals with the preparation of modified lead titanate, M-PT (M = Ca, La, Nd, Sm, Gd), by coprecipitating the oxalates of the different cations from an ethanol solution. The process parameters leading to both a very fine particle size coprecipitate as well as to deagglomerated calcined powder will be investigated. The densification process and microstructural development for the different additives will also be studied.

2. Experimental procedure

In this investigation the samples were prepared according to the flow diagram given in Fig. 1. The starting raw materials ($> 99.9\%$) were PbO, $Ti(C_4H_9O)_4$ C_4H_9OH, $La(NO_3)_3xH_2O$, $Ca(NO_3)_2 4H_2O$, WO_3,
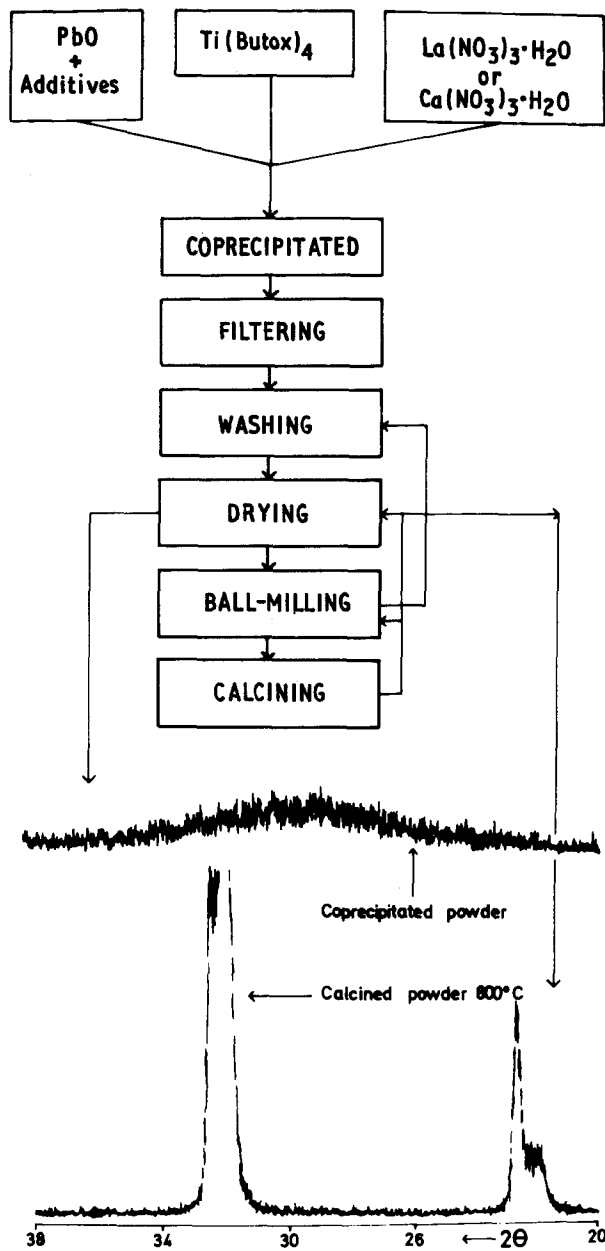
Figure 1 Flow diagram for the preparation of modified lead titanates, and X-ray diffraction patterns of the washed coprecipitated and calcined PT oxalates.

$CoCO_3$ and $MnCO_3$, and the synthesis was carried out from the required mixtures leading to an oxidic compound of the composition $(Pb_{0.76}Ca_{0.24})((Co_{0.5}W_{0.5})_{0.04}Ti_{0.96})O_3$ or $(Pb_{0.88}La_{0.08})(Ti_{0.98}Mn_{0.02})O_3$ in the case of calcium or lanthanum-modified $PbTiO_3$ ceramics, respectively. Batches of 100 g, based on the weight of final modified PT powder, were prepared by weighing the required amounts of PbO + $MnCO_3$ or PbO + $CoCO_3$ + WO_3, and transferring the powders to an ordinary blender containing the appropriate amount of oxalic acid dissolved in an ethanol–water mixture. The required amounts of titanium tetrabutoxide and lanthanum or calcium nitrates were also dissolved in ethanol by blending. The corresponding mixture was then added drop-wise to the blender containing the PbO–oxalic acid mixture by stirring. As the tetrabutoxide–nitrate solution was added, the titanium tetrabutoxide was, in a first step, hydrolysed by the water of the oxalic acid solution and, simultaneously, the lead oxide reacts with this precipitate to produce lead hydroxide, which further reacted with the oxalic acid to produce a final complex basic oxalate. The quantitative precipitation was achieved by adding an ammonia aqueous solution. The slurry was filtered and dried in an oven over night. The dried powder was milled with ethanol, filtered, and washed with ethanol several times and dried. After drying, the powder was calcined at 800° C for 3 h. After calcining the powder was attrition milled with ethanol, dried, granulated and isopressed at 200 MPa. Isothermal sintering was carried out between 1000 and 1200° C for different sintering times from 1 to 8 h.

Coprecipitated and calcined powders were characterized using BET, Coulter or Sedigraf, TEM, SEM and X-ray diffraction. The density of sintered samples was measured by the Archimedes method. Grain growth was studied on sintered, polished and thermally etched samples using SEM, and grain size was measured by the interception method [13]. Linear thermal expansion was measured by means of an automatic dilatometer.
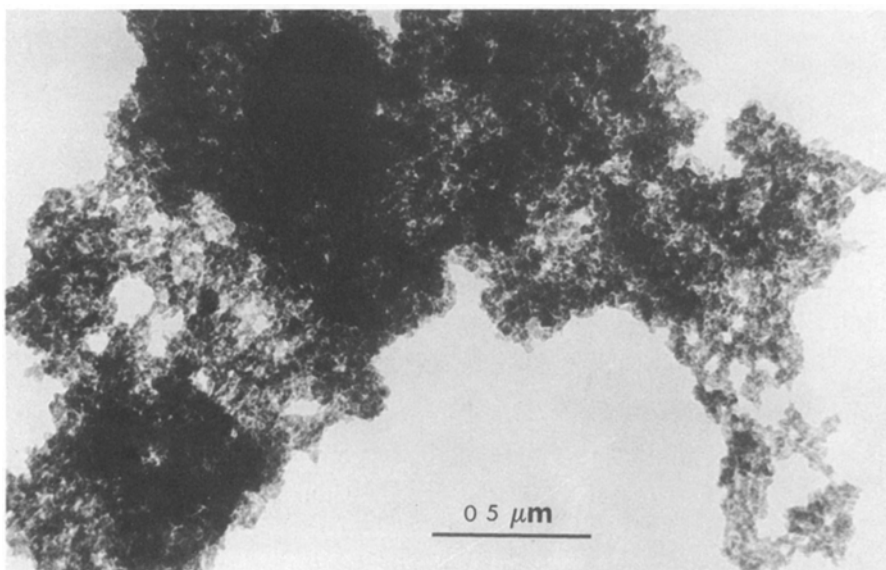

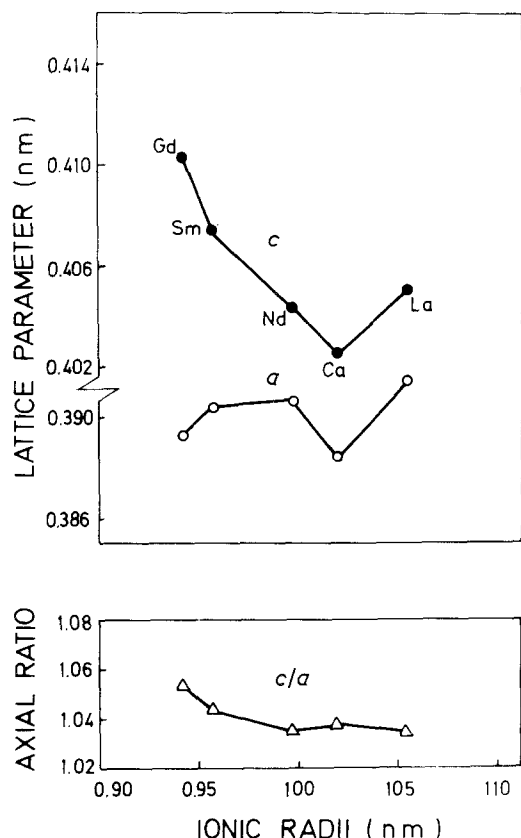*Figure 2* TEM picture of the amorphous modified PT oxalate.

Figure 3 Lattice constants and axial ratio for the modified lead titanates plotted against the ionic radii of the cations introduced.

3. Results and discussion

3.1. Powder characterization

As can be seen from Fig. 1, the powder was an amorphous oxalate after washing for several times with ethanol. The as-filtered powder showed a X-ray diffraction pattern corresponding to a crystalline phase mixture of an unidentified complex oxalate and ammonium oxalate. The BET surface area study showed that all the amorphous powders have a specific surface area ranging from 40 to 50 m^2 g^{-1}. Fig. 2 shows a typical TEM picture of the amorphous washed sample the morphology of which is representative of that observed for the different modified lead titanate precipitated powders. The primary particle

size could be obtained from the specific surface data to be around 44 nm in all cases, while the average particle size measured from the TEM observation was of ~ 32 nm. Although the amorphous sample was a well dispersed powder, however, its particle agglomeration state did not allow a very good precision in the particle measurements. X-ray diffraction patterns of the powders calcined at 800° C for 2 h were indexed as a tetragonal phase in all cases. Fig. 3a shows the variation of the a and c lattice parameters as a function of the ionic radius of the cation entering into the lead titanate perovskite structure. As can be seen, the substitution of Pb^{2+} by La^{3+} or Ca^{2+} introduced a strong reduction of the c parameter. On the other hand, no significative change was observed in the a parameter. As a consequence, the tetragonality, c/a ratio, of the modified lead titanate was strongly changed, as can be seen from Fig. 3b, compared with that of pure PbTiO$_3$ (c/a = 1.064). These results enable one to establish that a solid solution was formed in the CaO–PbTiO$_3$ and Ln$_2$O$_3$–PbTiO$_3$ systems, respectively.

3.2. Thermal expansion measurements

As a consequence of the strong change taking place in lattice parameters at the phase transition temperature, a large microcracking could be present in the modified lead titanate ceramic which, on the other hand, would influence their d–p properties. In this way a knowledge of their thermal expansion is extremely important. Fig. 4 shows the linear thermal expansion curves for different modified lead titanates. Compared with that of pure lead titanate (α = $-6 \times 10^{-6\circ}$C^{-1}) the linear thermal expansion coefficient of these ceramics are much smaller ranging from $-0.6 \times 10^{-6\circ}$C^{-1} for La–PbTiO$_3$ to -5.48×10^{-6}C^{-1} for Sm–PbTiO$_3$ in the tetragonal region. In the case of Ca–PbTiO$_3$ the linear thermal expansion coefficient was $-2.5 \times 10^{-6\circ}$C^{-1} in the range 25 to 250° C. The linear thermal expansion coefficient for Gd–PbTiO$_3$ was very similar to that of pure PbTiO$_3$ which provoked a disruption of the ceramics at room temperature. It means that the high anisotropic thermal expansion observed below the phase transition results in a large microcracking of
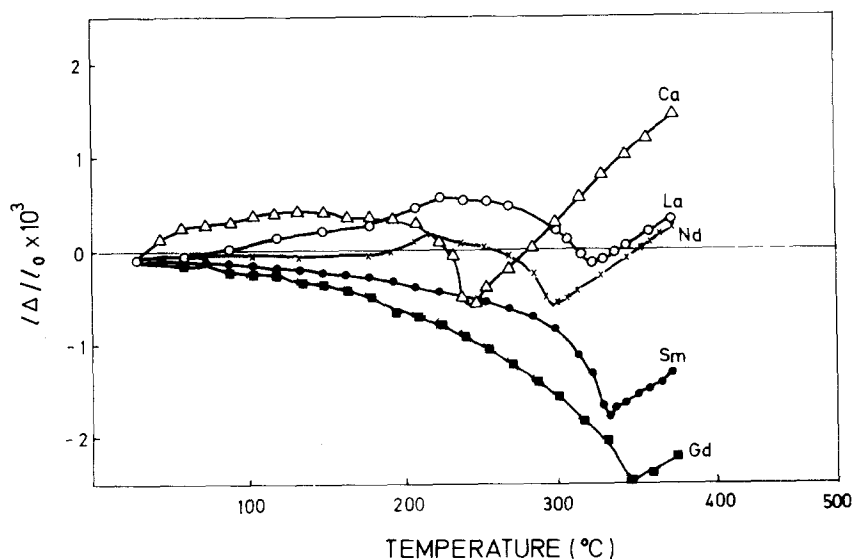

Figure 4 Linear thermal expansion of calcium- and lanthanide modified lead titanates.
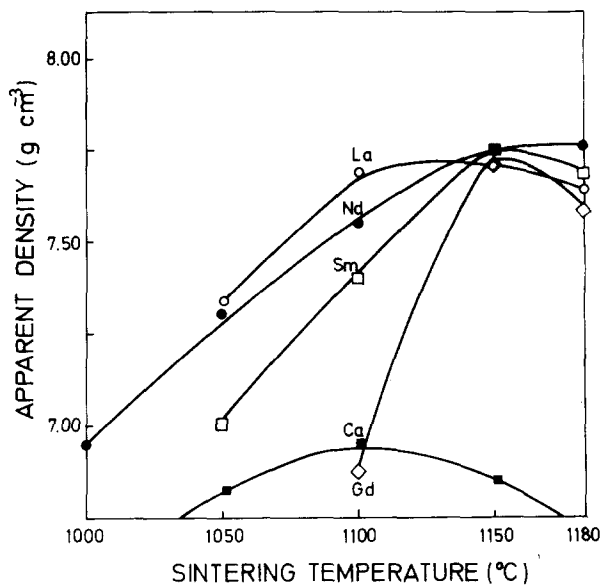
Figure 5 Density of modified PT as a function of sintering temperature.

the best sintering temperature was found to be 1100° C. Beyond those temperatures the density falls rapidly with increasing temperature. In all cases the densification was greater than 98% theoretical density at the optimum temperature.

The effect of the sintering time was carried out at those temperatures at which a maximum density was found, i.e. at 1150 and 1100° C for the lanthanum-modified lead titanate and Ca–PbTiO$_3$ ceramics, respectively. Fig. 6a shows the effect of time on the density of lanthanum-modified lead titanate samples. The sintered density increased with time reaching a limiting density for 5 h of heat-treatment. The highest density was achieved with Nd– and Sm–PbTiO$_3$ samples ($\geq$98% theoretical density), although in all the cases the density was sufficiently high to give an impervious material. As can be seen, most of the curves shows a similar slope which indicates that the different lanthanides added did not influence the densification kinetics over the period of time studied; however, the strong slope change produced above 5 h of heat-treatment means that all the additives enhanced the densification during the earlier stages of the sintering process.

Fig. 6b shows the effect of time on sintered density in the case of calcium-modified lead titanate samples, and a similar trend to that of the Ln–PbTiO$_3$ sample was found. The sintered density increased with time reaching a limiting value at 3 h heat-treatment. As before, a slope change took place with extended time and sintered density decreased. A sintered density value as high as 99% theoretical density was achieved for a temperature as low as 1100° C.

the ceramics. On the other hand, it seems that a critical c/a ratio of $\sim$1.050 $\pm$ 0.002 above which a catastrophic failure in the lanthanum-modified lead titanate ceramics is to exist. In the case of the CaO–PbTiO$_3$ ceramics such a critical c/a ratio was located to be around 1.041 $\pm$ 0.001. Samples with a c/a ratio greater than those mentioned above showed a large microcracking and, in some cases, a strong fragility. The possibility of a spontaneous strain induced at the phase transition temperature could also be taken into account [14].

3.3 Sintering

In an attempt to find both the optimum temperature and time of sintering a series of samples was sintered under various conditions. It must be mentioned that the sintering was performed in air and the samples were embedded within powder of the same composition. Fig. 5 shows the bulk density as a function of sintering temperature for a soaking time of 2 h. The sintering rate increased with increasing temperature in the order: Gd^{3+} > Sm^{3+} > Nd^{3+} > La^{3+}. Nevertheless, an identical optimum sintering temperature, 1150° C, was found for the lanthanum-modified lead titanate ceramics. In the case of calcium-modified lead titanate

3.4. Microstructural development

In an attempt to elucidate the reason for the density decreasing above both a critical temperature and time of sintering, an evaluation of the microstructural development was carried out. Fig. 7 shows a picture of the microstructural development in all the modified lead titanate ceramics at the optimum temperature and time of sintering. As can be seen, the effect of the different substituting cations on the grain size of PbTiO$_3$ was that of inhibiting the grain growth, regardless of the substituted cation. In all cases the
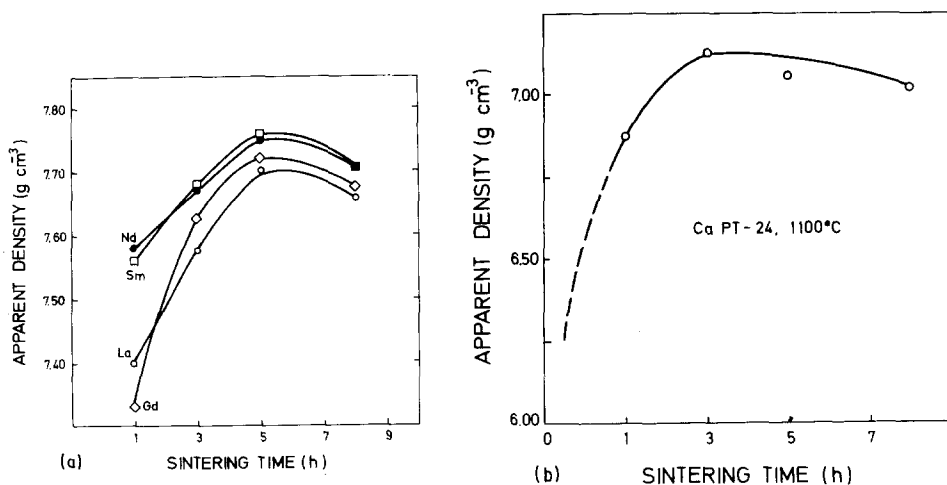

Figure 6 Effect of sintering time on density for (a) lanthanide-modified PT at 1150° C, and (b) calcium-modified PT at 1100° C.
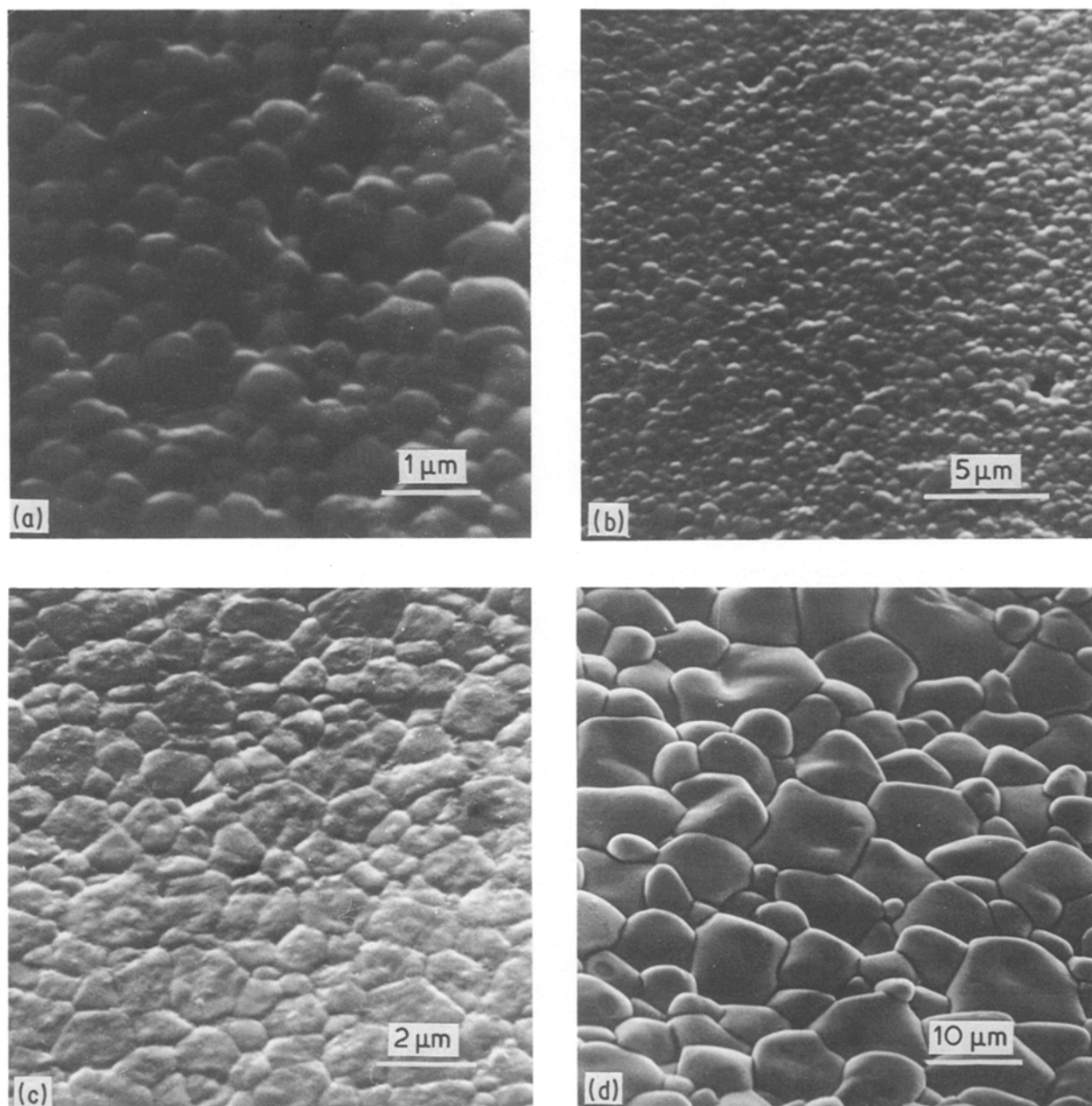
Figure 7 Microstructure of Ln–PT and Ca–PT sintered at 1150 and 1100° C, respectively; (a) Ln–PT, (b) Nd–PT, (c) Sm–PT, and (d) Ca–PT.

grain size was smaller than 1 μm and neither grain–grain separation nor intergranular microcracking were present. Only in the case of the calcium-modified lead titanate, in which the grain size was near 10 μm, were some microdomains detected on the grain surface.

Above the selected temperatures and times of sintering, a common feature was found in the microstructure of the different modified lead titanates. At the zones near the surface of the samples a bimodal grain-size distribution was present, and grain sizes greater than 5 μm were measured. These two grain sizes provoked a large microcracking and internal stresses in the samples, this being a probable cause for the decrease in the sintered density. If it is assumed that the modified lead titanate sintering process takes place via a transient liquid phase, then such apparently anomalous microstructural features could be explained as follows: (a) Above the selected sintering temperatures the activity of PbO becomes considerable and, probably, a diffusion towards the grain boundary

takes place. (b) For extended periods of time, the PbO located at the grain boundaries diffuses to the surface sample which, being in contact with embedding powder, equilibrate the internal and external PbO vapour pressure. In such a case the concentration of PbO in the vicinity of the sample surface is higher than in the centre of the sample and, therefore, the grain-growth process is favoured by the presence of a liquid phase.

Another probable cause for the density decrease could be the influence of the grain size on the c/a ratio of the modified lead titanate. If this is so, then the internal stresses produced by a nonuniform grain-size distribution could give rise to the formation of a large microcracking in the sample and, as a consequence, a density decrease. Fig. 8 shows the microstructural development as a function of the sintering time at 1150° C for samarium-modified lead titanate. As can be seen, the grain size developed was in the range ~ 0.5 to 1 μm, and it can also be observed that beyond
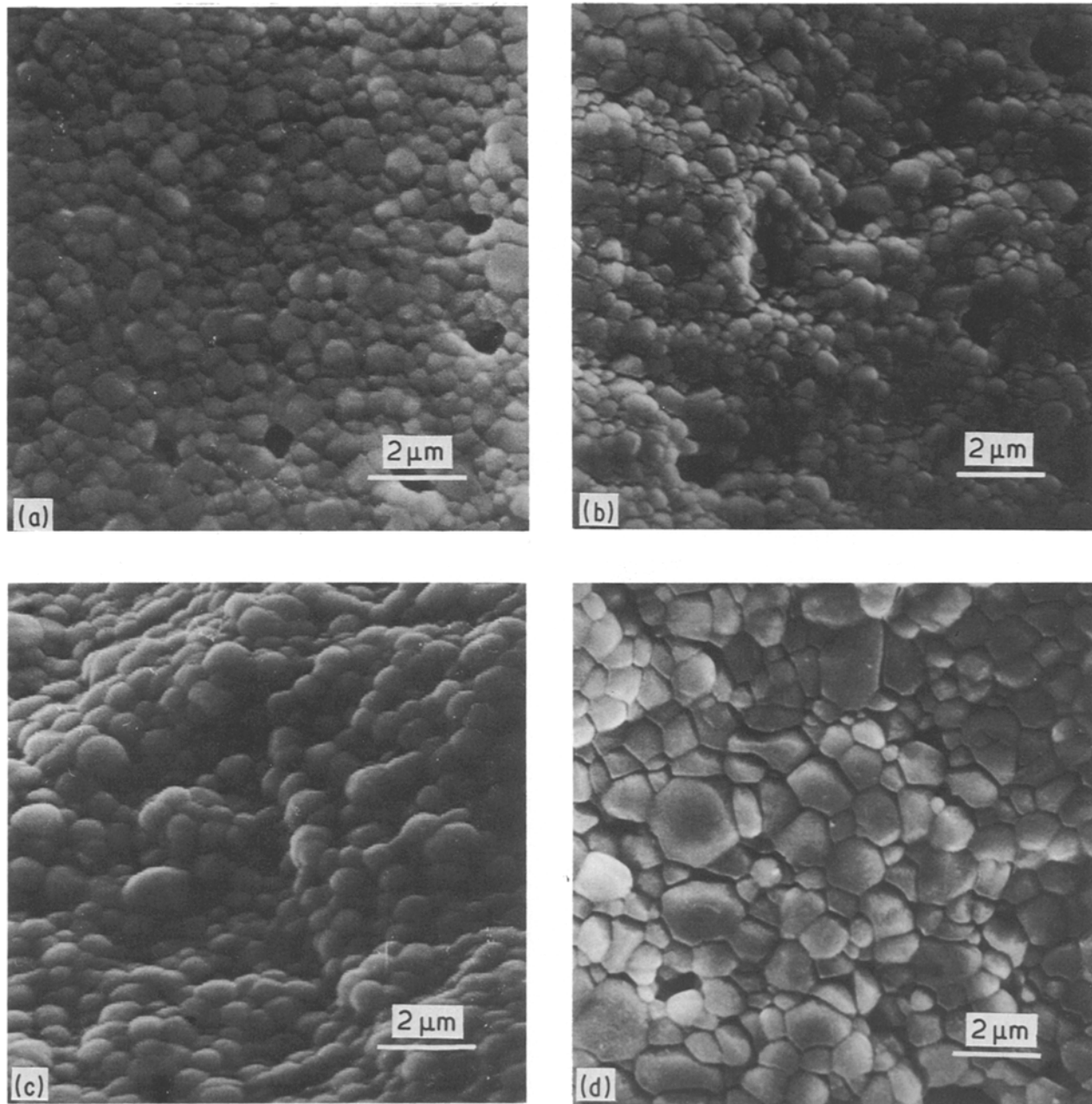
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Figure 8 Microstructural development in Sm–PT with sintering time at 1150° C. (a) 1 h, (b) 3 h, (c) 5 h, (d) 8 h.

5 h heat-treatment many cracks along the grain boundaries are formed. Fig. 9 shows the variation of c/a ratio as a function of grain size at room temperature. The tetragonal distortion of the perovskite phase unit-cell below the transition temperature decreases with increasing grain size. However, the changes in the lattice constants are different for the a-axis and the c-axis. While the c-axis strongly decreased the a-axis hardly varied. This a- and c-axis variation results in an averaged c/a decrease. This means that the sample microstructure is compressed in the c-axis direction and tensioned in the two a-axes directions. As a consequence a microcracking with the formation of an additional porosity was present in the microstructure, and it will be more evident if the grain size distribution is not very uniform, see Fig. 8d. These results are in contradiction with those reported by Buessem *et al.* [15, 16], in which an uncracked BaTiO₃ microstructure was obtained when the grain size was below ~ 1 μm. Keizer and Burggraaf [17] also reported that the c/a
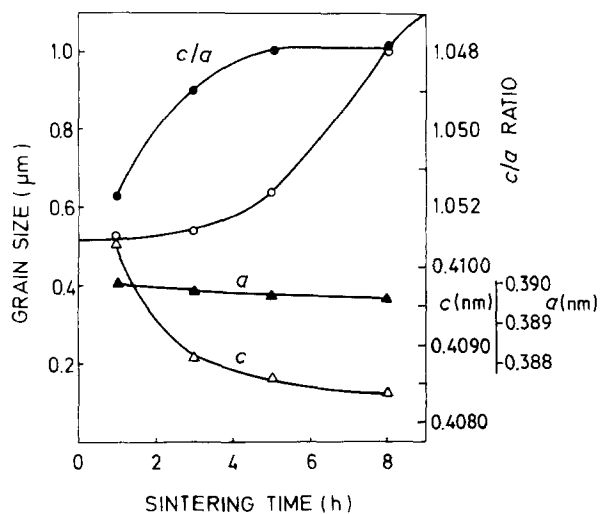

Figure 9 Variation of the lattice parameters and c/a ratio as a function of grain size.

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ratio diminished with decreasing grain size in two lanthanum-modified lead titanates sintered at different temperatures, and with very differently developed grain sizes. In our case it could be assumed that for a short sintering time (1 h) at 1150°C the Sm–PT solid solution was not completed and, if this is so, the c/a ratio could be greater than that corresponding to an equilibrium phase. In such a case the c/a ratio will decrease with increasing grain size up to a c/a value corresponding to that of the well-formed Sm–PT solid solution ($c/a = 1.048$), which is reached for a critical grain size of $0.65\,\mu m$ at 5 h heat-treatment. Beyond that grain size, the c/a ratio will probably increase, and an extensive microcracking in the microstructure will take place. Such a situation must probably be present for grain sizes greater than 1 μm as reported by Keizer and Burggraaf [17].

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