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Characterization of modified $PbTiO_3$ ceramic particles by statistical treatment of their size distribution

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Microstructural characteristics of (Pb, Ca)TiO_3 piezoelectric ceramic particles have been deduced from computer analysis of their images and the corresponding statistical treatment of the data obtained. It is intended that this study should be used as a nexus, or link, between the geometrical parameters of these particles and some of their physical properties.

1. Introduction

The search for materials with new and/or optimized properties leads invariably to their study by means of microstructural concepts [1], an area of knowledge that deals with establishing a relationship between the geometrical parameters of the microstructure and the physical properties of the materials.

In general, the microstructure of a material is defined by the number and identification of the corresponding phases, the amount and the characteristics (particle size and shape, orientation, etc.) of each phase. It is relatively easy to measure and express these parameters by using the so-called global variables [2] and statistical science as a nexus, or link, between these parameters and the behaviour of the end material. This treatment acquires a special interest in the development of polyphase systems in composites. Traditionally, these materials have been used because of the structural advantages of their mechanical properties. However, recently they have begun to find a wide field of application in the electronics industry [3]. Within the electroceramic composites, biphase materials in which one of the phases is formed by ceramic particles [4] are noticeable. To date, the study of this kind of precursor has been directed to the processing [5], without paying attention to characterization studies of the whole particle as an operative unit, which is of interest for previous ceramic studies, and for their incorporation in composites.

This work is directed to the development of a model which gives quantitative results about size, densification and other information on the conformation mechanisms in (Pb, Ca)TiO_3 particles [6], which allows their modification and therefore the preestablishment of differentiated microstructures.

2. Experimental procedures

2.1. Processing

The chemical composition of the particles obtained [7] is as follows:

$$[(Pb_{0.76}Ca_{0.24})(Co_{0.5}W_{0.5})_{0.04}Ti_{0.96}]O_3 + 1\%\ MnO\ (PTC)$$

A mixture of high purity oxides and carbonates was reactivated at a suitable point of the process by adding HNO_3 [8]. The dried chemical precursor presents a high degree of agglomeration which makes possible grinding and sieving, and allows us to obtain particles

TABLE I Log size distribution of ceramic particles

Number of interval (log particle size)	Particle size range ($\times 10^{-1}$ mm^2)	Percentage in range				
		1050° C, 6 min	1050° C, 12 min	1050° C, 30 min	1050° C, 60 min	1050° C, 180 min
1[(−1.92)–(−1.77)]	0.12–0.17	0.0	0.5	0.3	0.0	0.0
2[(−1.77)–(−1.62)]	0.17–0.24	0.7	0.0	0.3	0.0	0.0
3[(−1.62)–(−1.48)]	0.24–0.33	1.4	0.5	0.0	0.3	0.0
4[(−1.48)–(−1.33)]	0.33–0.47	4.0	0.8	3.0	1.0	1.3
5[(−1.33)–(−1.19)]	0.47–0.65	6.0	1.8	7.6	3.4	6.0
6[(−1.19)–(−1.04)]	0.65–0.92	10.5	7.3	16.4	7.8	8.7
7[(−1.04)–(−0.89)]	0.92–1.28	19.9	19.1	24.3	14.9	18.4
8[(−0.89)–(−0.74)]	1.28–1.80	22.1	27.2	26.2	23.6	27.1
9[(−0.74)–(−0.60)]	1.80–2.52	15.7	25.3	12.8	22.5	19.1
10[(−0.60)–(−0.45)]	2.52–3.52	10.0	9.4	6.6	15.7	12.7
11[(−0.45)–(−0.31)]	3.52–4.93	7.1	5.7	1.7	7.1	4.4
12[(−0.31)–(−0.16)]	4.93–6.90	2.2	2.4	0.8	3.4	2.0
13[(−0.16)–(−0.01)]	6.90–9.67	0.4	0.0	0.0	0.3	0.3
14[(−0.01)–(−0.13)]	9.67–13.54	0.0	0.0	0.0	0.0	0.0

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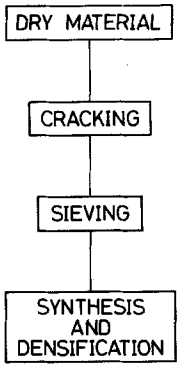

Figure 1 Processing of ceramic particles.

of different sizes (Fig. 1). The 0.30 to 0.80 mm fraction was selected to be studied. The synthesis and sintering (densification) was carried out by firing [9] in an electric furnace, in an air atmosphere, at 1050° C and a heating rate of about 8° C min^{-1} and soaking periods of 6, 12, 30, 60 and 180 min.

The microstructures which developed in these ceramic particles were studied by scanning electron microscopy (SEM).

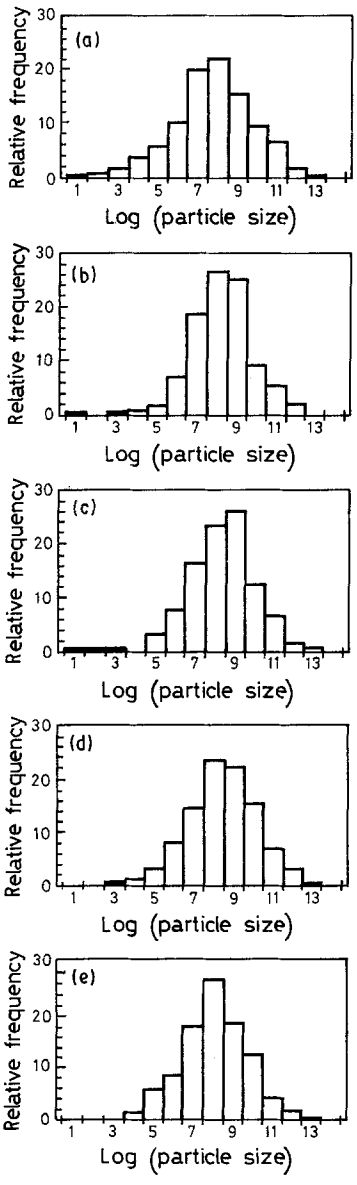

Figure 2 Log size distribution of ceramic particles. All at 1050° C; (a) 12 min; (b) 6 min; (c) 30 min; (d) 60 min; (e) 180 min.

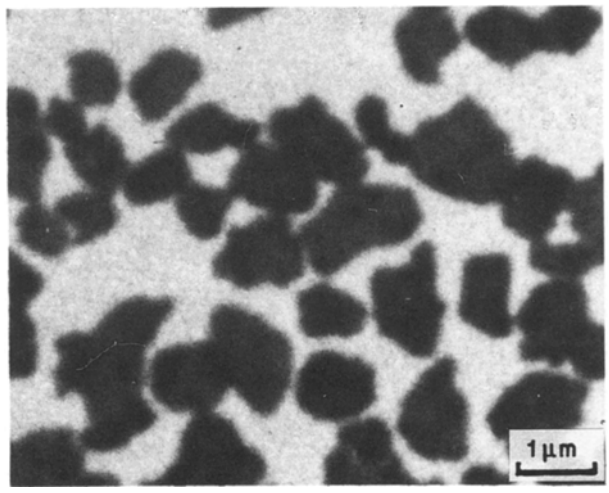

Figure 3 Photograph of (Pb, Ca)TiO_3 particles.

2.2. Experimental techniques

On photographs of the fired PTC particles, magnified 16 times, the areas of 400 specimens were measured and the logarithms of these areas classified into 14 intervals (Table I), by means of a computer calculus program. From the classified data, the corresponding relative percentage frequency of distributions (Fig. 2) and the probability distribution functions were drawn.

3. Results and discussion

The above chemical process allowed us to obtain particles of the PbO–CaO–TiO_2 system with equivalent spherical diameters ranging between 0.30 and 0.80 mm, and after synthesis and sintering provided (Pb, Ca)TiO_3 piezoelectric ceramic precursors with a tetragonal distorsion of c/a = 1.040 and a morphology

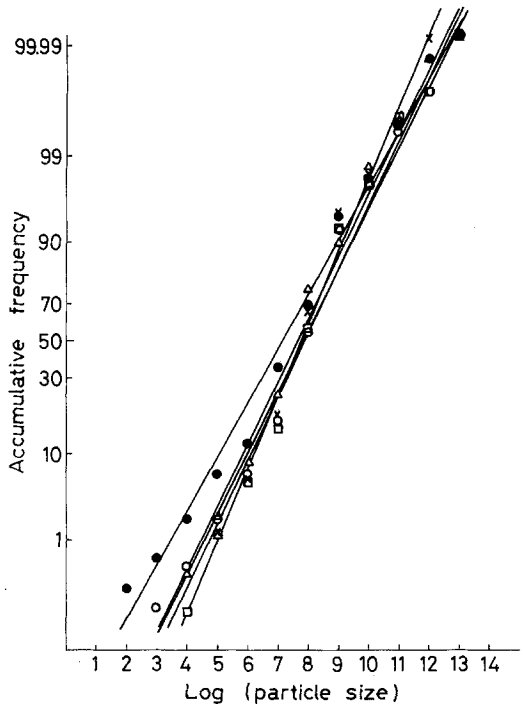

Figure 4 Probability distribution functions of log size of ceramic particles.
●, 6 min, $y = -66.2 + 19.0x^2$, $r^2 = 0.99$
× 12 min, $y = -20.5 + 14.2x$, $r^2 = 0.99$
□ 30 min, $y = -50.6 + 16.7x$, $r^2 = 0.99$
○ 60 min, $y = -43.6 + 16.9x$, $r^2 = 0.99$
△ 180 min, $y = -44.3 + 16.6x$, $r^2 = 0.99$.

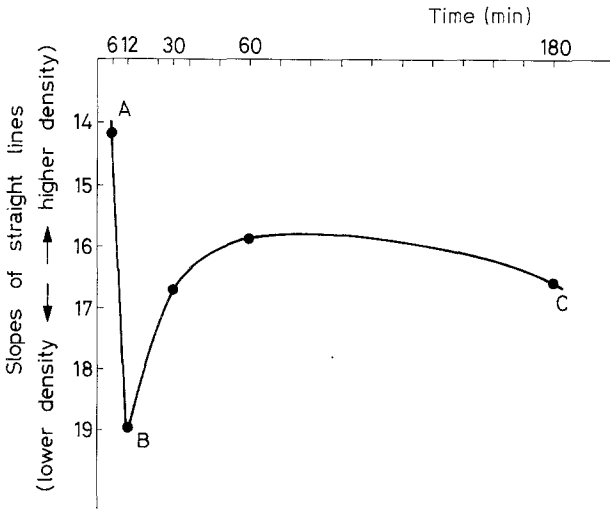

Figure 5 Variation of slope of straight line against firing time at 1050° C.

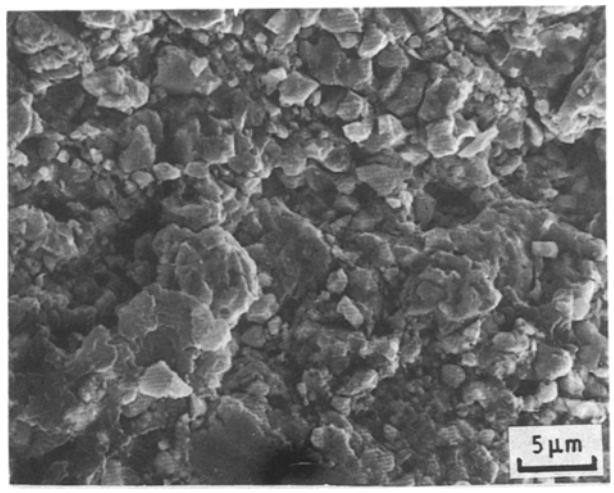

Figure 6 Micrograph of (Pb, Ca)TiO_3 ceramic particles (1050° C, 6 min).

as shown in Fig. 3. The difficulty of characterizing the size distributions and the densification of the particles, and the interest of these results for the design of composites has led to the preparation of a computer calculus program. This program determines and draws the 10 g particle size distribution by means of the particle images. Normal distributions were obtained (Fig. 2). However the obtained distributions are asymmetrical, and the tendency of this asymmetry suggests qualitatively how the densification of the particles evolves. The asymmetry towards the right suggests a decrease in particle size and therefore an increase of densification. The asymmetry towards the left suggests an increase in particle size and consequently a decrease of densification.

These concepts can be semi-quantified by drawing the probability distribution functions of the particle sizes. The slopes of the straight lines obtained (Fig. 4) are related to the asymmetry of the particle size distribution, and therefore to the densification of the material. The lower the slope, the greater the asymmetry towards the left of the histogram, and consequently the densification decreases. On the other hand, the higher the slope, the higher the densification. Fig. 5 shows the evolution of the densification of the particles with soaking time by considering the relationship between densification and the slopes of the straight lines.

This type of curve has already been found for (Pb, Ca)TiO_3 monolithic ceramics, and it is characteristic of systems in which one component has a low melting point [10] as it happens in this case ($T_{fPbO} \sim$ 880° C). This fact gives rise to the first part of the curve (Fig. 5) that presents a decrease in densification, which is due to the volatility of the PbO; if the soaking period is longer, the sintering mechanisms dominate the process and an increase of densification can be observed. For a very long soaking period, degradation of the particles for overfiring occurs.

Two different types of microstructure, corresponding to the parts beside the minimum (B) of the curve of Fig. 5, are evident. The micrograph in Fig. 6 shows the microstructure found at the left of the minimum (part AB), and that of Fig. 7 shows the microstructure at the right of the minimum (part BC). The former is due to the fact that the system suffers a slight volatility of PbO and a consolidation process of the grains originated in the previous synthesis, with supposed and reduced growth, because of the incidence of a liquid phase. According to Fig. 7, the second part of the curve presents a sintering mechanism which condenses at a high particle shrinkage accompanied by the densification of the primary grains and the coupling of the smaller new secondary ones. Consequently, as a result of this mechanism a gradual and increasing densification of the material takes place. In short, a suitable interpretation of the former curve, which is obtained by means of a statistical treatment of the areas of a number of (Pb, Ca)TiO_3 ceramic particles, provides enough information to establish the sintering conditions which lead to PTC particles with different microstructures. In this study, ceramic particles which may be incorporated as precursors in designed composites can be characterized, giving a certain degree of control of the expected electromechanical response of these materials.

4. Conclusions

Ceramic characterization of (Pb, Ca)TiO_3 particles

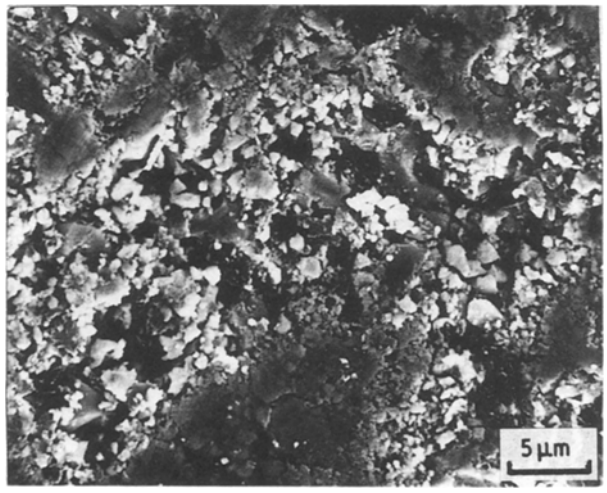

Figure 7 Micrograph of (Pb, Ca)TiO_3 ceramic particles (1050° C, 60 min).

has been carried out using a statistical treatment of the particle sizes. These were obtained by means of a computer calculation program, which determines the log particle size distributions.

Normal distributions were obtained. Their corresponding probability distribution functions allows us to explain theoretically the behaviour of the densification process of the particles. Additional information about the firing conditions that lead to ceramic particles having the same chemical composition but different microstructures was obtained.

In this way, it is possible to control the ceramic properties of the (Pb, Ca)TiO_3 particles intended for use as precursors in piezoelectric composites.

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