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Mechanism of formation of $MTiO_3$ ($M = Sr$ or Ba) by the gel method

M. I. DIAZ-GUEMES, T. GONZÁLEZ CARREÑO, C. J. SERNA
Instituto de Ciencia de Materiales (C) Serrano, 115 dpdo, Madrid-28006, Spain
J. M. PALACIOS
Instituto de Química-Física (Rocasolano) Serrano, 117, Madrid-28006, Spain

Strontium and barium titanates were obtained at room temperature and 60° C, respectively, by the gel method. Factors affecting the formation of the titanates, such as the nature of the reactants, temperature, pH and time were studied. It is shown that the mechanism of formation occurs through diffusion of alkaline earth cations inside the titanium dioxide (TiO_2) gel particles. Thus, particle size and shape of the titanates can be controlled by determining the TiO_2 gel characteristics. This is illustrated by synthesizing the titanates with spherical submicron monosized particles.

1. Introduction

Barium and strontium titanates ($MTiO_3$; $M = Ba$ or Sr), important solids in the electronic ceramic industry, are usually obtained through two different types of reactions. The first type comprises the classical ceramic method in which mechanical mixing of MO or MCO_3 and TiO_2 is carried out along with progressive thermal treatment [1, 2]. Here, the formation of $MTiO_3$ occurs through a solid state reaction in which counter-diffusion of the metal cations must occur inside the oxygen lattice. Temperatures $> 1000°$ C are needed in order to speed the process. A second method to prepare $MTiO_3$ consists of the thermal decomposition of an organic precursor in which the cations M and Ti are already in close proximity. By this method, metal diffusion is avoided and the formation temperature of the perovskites lowered to about 600° C; this is probably the temperature needed for the formation of the oxygen perovskite lattice. The pyrolysis of alkaline earth titanyl oxalates [3], some metallo–organic compounds [4] and the decomposition of peroxidic complexes [5] can be included under this method.

Several reports based on the works of Flaschen [6], and Mazdiyasni *et al.* [7], have appeared on the low-temperature formation of $MTiO_3$ by gel methods [8–11]. Thus, crystalline barium and strontium titanates can be obtained during the hydrolysis of a titanium solution in the presence of barium or strontium hydroxide at temperatures $< 80°$ C. The objective of this paper is to analyse the experimental conditions for the formation of both titanates in solution. In addition, their mechanism of formation is explained by using well-defined TiO_2 spheres.

2. Experimental procedure

All chemicals were of the highest commercially available purity. Generally, $MTiO_3$ was obtained by hydrolysis of an alcoholic solution of $Ti(OC_2H_5)_4$ in concentrated solutions of barium or strontium hydroxide. The reaction was carried out in Teflon hydrothermal vessels which can be heated to 200° C. To ensure a complete reaction, the alkaline earth metals (Ba or Sr) were added in addition to stoichiometry. After the reaction, the products were filtered and washed with diluted citric acid to remove any excess unreacted MCO_3 and finally dried at 60° C.

The formation of $MTiO_3$ carried out in this way can be considered as a one step procedure which can be written:

$$Ti(OC_2H_5)_4 + H_2O + M(OH)_2 \rightarrow MTiO_3 + 4C_2H_5OH \quad (1)$$

Under these conditions, the factors affecting the formation of $MTiO_3$ were investigated (i.e. the nature of reactants, temperature, pH and time). The formation of $MTiO_3$ can also be carried out by a two-step procedure, according to the reaction:

$$Ti(OC_2H_5)_4 + 2H_2O \rightarrow TiO_2(gel) + 4C_2H_5OH \quad (2)$$

$$TiO_2(gel) + M(OH)_2 \rightarrow MTiO_3 + H_2O \quad (3)$$

In order to investigate the mechanism of formation, experiments were carried out through this second procedure using well-defined TiO_2 particles [11–13], produced by hydrolysis of titanium tetraethoxide in alcohol solution (0.2 M) with an $H_2O/Ti(OC_2H_5)_4$ molar ratio of ca. 4.51. The TiO_2 gel formed was allowed to react with barium or strontium hydroxide solutions in the hydrothermal vessel at 100° C in order to ensure titanate formation.

Identification of the products were carried out by X-ray powder diffraction (Philips PW 1710 diffractometer) and IR spectroscopy (Perkin–Elmer 580B spectrometer). Particle size and shape were analysed under a scanning electron microscope (SEM) (ISI DS-130) equipped with energy-dispersion X-ray analysis (EDS).

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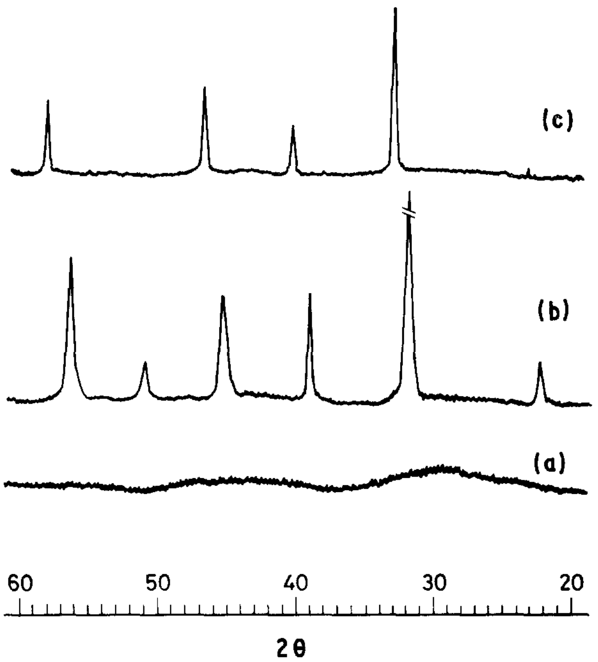

Figure 1 X-ray diffraction patterns of the powders obtained during the hydrolysis of $Ti(OC_2H_5)_4$ at room temperature in the presence of: (a) barium hydroxide solution (0.12 M); (b) sample (a) heated to 600° C during 12 h; (c) strontium hydroxide solution (0.16 M).

3. Results and discussion

3.1. Effect of several variables

Most of the experiments were carried out by adding the organometallic compound ($Ti(OC_2H_5)_4$) directly to the alkaline earth hydroxides. Crystalline $SrTiO_3$ was obtained at room temperature almost immediately by this reaction (Fig. 1c). The hydrolysis of the titanium alkoxide in the presence of barium hydroxide at room temperature however resulted in amorphous $BaTiO_3$ (Fig. 1a) which remained amorphous for a long time. The amorphous precipitate, once separated from the solution, needs temperatures of about 600° C to produce crystalline $BaTiO_3$ (Fig. 1b). In these conditions, the reaction was not completely stoichiometric in agreement with similar observations made by Kiss *et al.* [8] who showed that for $BaTiO_3$ the reaction was stoichiometric only above 80° C. However, what was more important here was that the temperature needed to form crystalline $BaTiO_3$ ($\sim 600°$ C) parallelled the methods based on the thermal decomposition of organo-precursors. Thus, we concluded that the formation of a long-range perovskite oxygen structure by solid state reaction needed temperatures of $\sim 600°$ C, independent of the precursor used.

$BaTiO_3$ could be obtained with a rather good crystallinity after 2 h at 60° C (Fig. 2b), but the product obtained initially was amorphous, according to X-ray diffraction (Fig. 2a). However, longer periods of time did not improve the crystallinity of $BaTiO_3$ which remained unaltered (Fig. 3c). As expected, the reaction could be accelerated by increasing the temperature, crystalline $BaTiO_3$ being formed almost immediately at temperatures higher than 100° C.

Different tests were performed to verify whether the choice of reactants and conditions were optimal. It became evident that two factors influenced this reaction: the pH and the presence of carbonates which inhibited titanate formation. Thus, the water used for the solutions was preheated to eliminate CO_2 and later cooled in a CO_2-free atmosphere. Consequently, experiments conducted with alkaline earth carbonates did not form titanates.

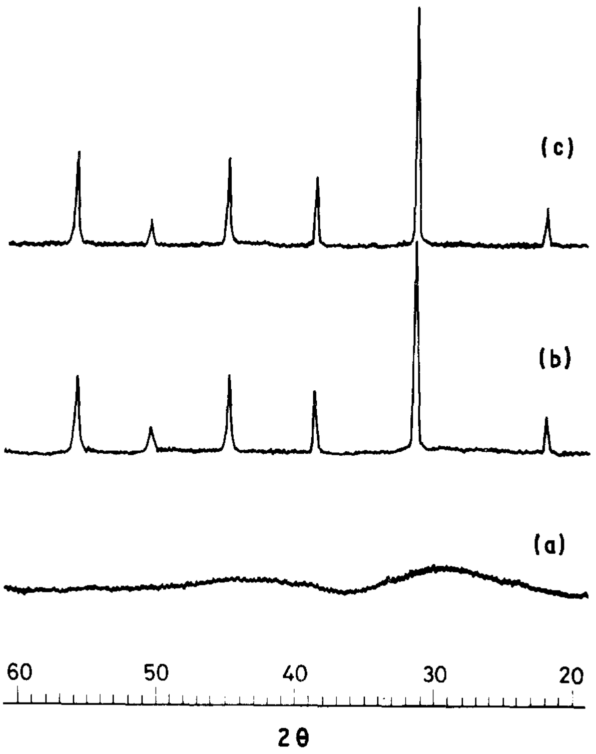

Figure 2 X-ray diffraction patterns of the powders obtained during the hydrolysis of $Ti(OC_2H_5)_4$ at 60° C in the presence of a barium hydroxide solution (0.12 M). (a) As initially formed; (b) after 2 h; (c) after 48 h.

The other important factor, pH, had to be maintained at pH > 11 for the reaction to occur. Thus experiments carried out with concentrations of barium hydroxide solution < 0.1 M were unsuccessful, since they resulted in a pH < 11. This observation explained, for example, why only TiO_2 gel was obtained in the presence of alkaline earth halides, since they produced neutral pH solutions. Therefore, it was concluded that a strongly alkaline environment was essential for the formation of the titanates.

The perovskite compounds could be formed under the same conditions, i.e. the gel was formed within the alkaline solution or in a different container and later transferred to the alkaline solution. The important difference in performing the reaction by the latter

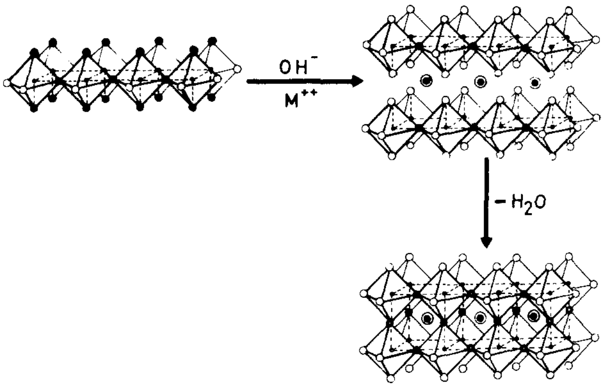

Figure 3 The mechanism of formation of $MTiO_3$ ($M = Ba^{2+}$ or Sr^{2+}) by the gel method. (●) H_2O; (○) OH^-; (◦) $O^=$; (·) Ti^{4+}; (⊙) M^{++}.

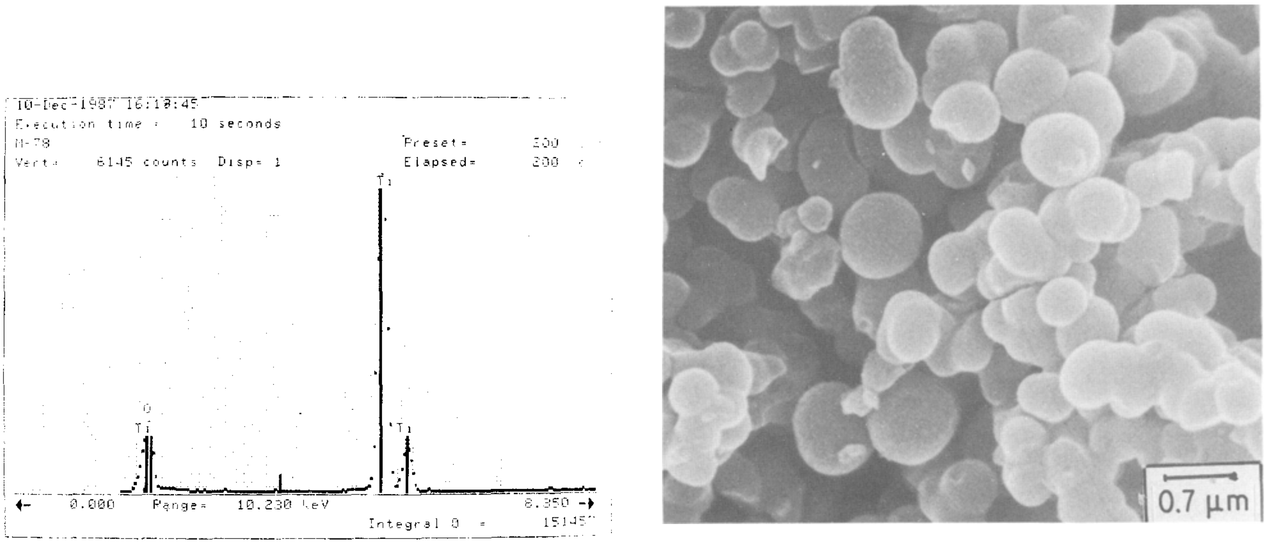

Figure 4 Scanning electron microscopy (SEM) micrograph and energy-dispersion X-ray analysis (EDS) of TiO_2 gel particles produced [12].

method was the ageing process that the TiO_2 gel suffers losing reactivity. In fact, TiO_2 gels immersed for 24 h in their own solution did not form titanates, even at 100° C. This result would also explain the lack of reactivity observed when anatase or rutile were used as sources of TiO_2 [9].

3.2. Mechanism of formation

The results in the previous section for the formation of $MTiO_3$ by the gel method and those already published [6–11] are explained by the mechanism of formation. Two types of mechanism can be postulated which fulfil most of the experimental results. The first is an acid–alkali reaction in which an anion of formula $Ti(OH)_6^{2-}$ is initially formed during the hydrolysis of the alkoxide and later neutralized by the alkaline earth cations. The reaction can be written:

$$Ti(OH)_6^{2-} + M^2 \rightarrow MTiO_3 + H_2O \qquad (4)$$

This acid–alkali mechanism has been suggested previously [8, 10, 11] and would fully account for the high pH sensitivity of the reaction. However, the differences observed between barium and strontium cannot easily be explained by this mechanism.

A second type of mechanism which would satisfy the experimental observations can also be proposed (Fig. 3). Initially, the hydrolysis of the organo-metallic titanium takes place forming a TiO_2 gel in which hydroxyl groups are absorbed giving a negative charge to the particles. Later, the alkaline earth cations diffuse inside the particles to counterbalance the negative charge. Finally, a condensation mechanism produces the tridimensional perovskite structure expelling water molecules.

In order to differentiate between both mechanisms crystalline $MTiO_3$ was synthesized by reaction (2), using well-defined TiO_2 gel spheres [12, 13]. A comparison of the morphological characteristics of the TiO_2 gel particles before (Fig. 4) and after the reaction with the solutions of strontium or barium hydroxides clearly showed that particle morphology had been preserved (Fig. 5). X-ray diffraction patterns of the reaction products showed that crystalline perovskite compounds had been obtained (data not shown).

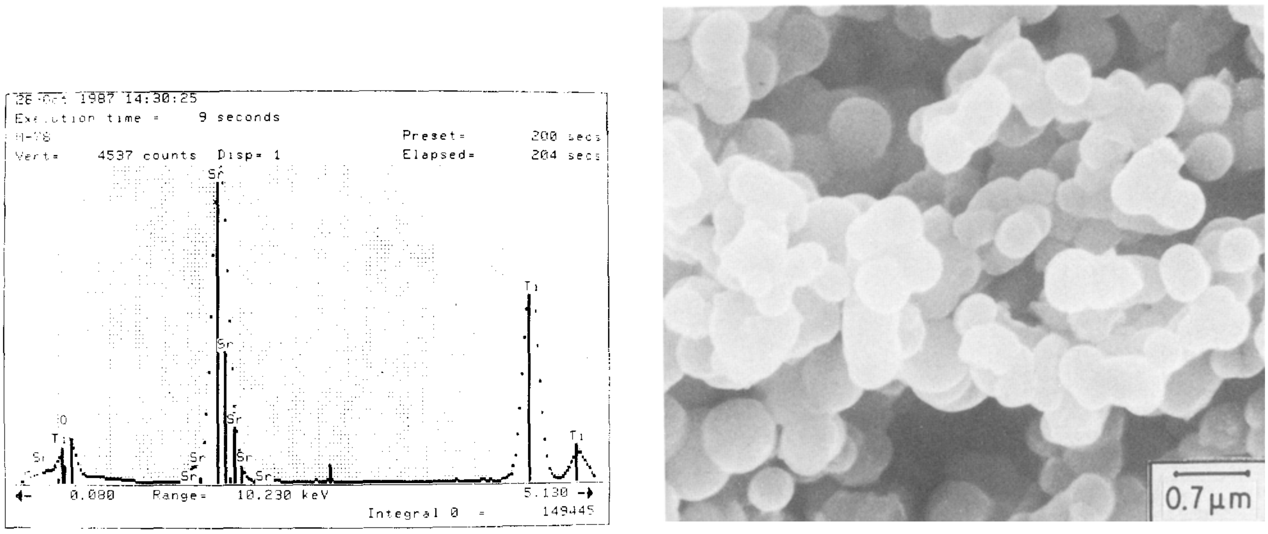

Figure 5 Scanning electron microscopy (SEM) micrograph and energy-dispersion X-ray analysis (EDS) of the $SrTiO_3$ formed by reaction of the TiO_2 particles of Fig. 4 with a solution of strontium hydroxide (0.16 M).

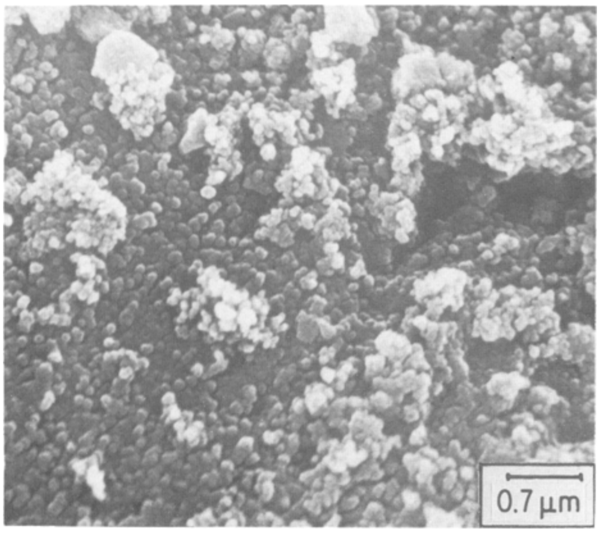

Figure 6 Scanning electron microscopy (SEM) micrograph of the $SrTiO_3$ formed according to reaction (1).

Even at single particle level, the EDS diagrams show that the alkaline earth metals have diffused inside the spherical TiO_2 particles forming the perovskite type compound (Fig. 5). Therefore, a diffusion mechanism is responsible for the formation of the perovskites produced by the gel method. By this mechanism, all the experimental results presented can be explained, particularly the differences in behaviour between barium and strontium.

In this way, the particle size of the titanates is determined mainly by the characteristic of the TiO_2 gel initially formed. The titanates obtained by the one-step reaction procedure (Fig. 6) possess particle sizes clearly smaller than those obtained by forming the TiO_2 gel separately (Fig. 5).

Therefore, we concluded that the formation of $MTiO_3$ compounds occurs through a diffusion mechanism of the alkaline earth cations into the TiO_2 gel particles. Knowing the mechanism, particle size and shape of the perovskite titanates, can now be controlled [14] which has a tremendous importance in determining the dielectric behaviour of these materials [15].

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