JOURNAL OF MATERIALS SCIENCE 18 (1983) 3041–3046

Synthesis reaction of metatitanate $BaTiO_3$

Part 1 *Effect of the gaseous atmosphere upon the thermal evolution of the system $BaCO_3$-TiO_2*

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Thermogravimetric and X-ray diffraction analysis of the reaction mixture, during the synthesis of barium metatitanate $BaTiO_3$ from $BaCO_3$ and TiO_2 allowed clarification of the transformation time and the role of the reaction environment: in air, the occurrence of $BaTiO_3$ is in competition with that of orthotitanate Ba_2TiO_4. The latter forms between 25 and 95% of the transformation of the initial mixture by reaction between $BaCO_3$ and $BaTiO_3$. Under vacuum, metatitanate is not detected before 70% of transformation of the initial mixture. The orthotitanate occurs alone, oxide BaO produced by the decomposition of the carbonate and replaces it in the reaction syntheses. In CO_2, the synthesis of $BaTiO_3$ competes with the formation of a phase other than Ba_2TiO_4 but whose behaviour during calcination is comparable to that of the orthotitanate.

1. Introduction

The performance of the industrial synthesis of barium metatitanate $BaTiO_3$ by reaction, at high temperature, between carbonate $BaCO_3$ and titanium oxide TiO_2 is often lessened by the simultaneous formation of other titanates. Systematic analysis of industrial calcines showed that orthotitanate Ba_2TiO_4 occurs most frequently and is present in large amounts: its presence harms the electrical properties of high constant dielectric ceramics, of which $BaTiO_3$ is the main constituent.

Numerous factors must be controlled to obtain a metatitanate of acceptable purity, i.e. quality of raw materials, granulometry, mixture homogeneity and nature of the reaction atmosphere.

Starting with the raw materials which are used in industry and treating them under conditions we tried to approach the conditions for the formation of metatitanate and orthotitanate during calcination and we have examined the extent to which the reaction atmosphere affects the formation of Ba_2TiO_4.

Earlier studies in this field shall be recalled briefly. Several assumptions were made to explain the formation of the two titanates. According to Turlier [1] and Trzebiatowski *et al.* [2] $BaTiO_3$ and Ba_2TiO_4 would form simultaneously by a reaction between the carbonate and the oxide.

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \qquad (1)$$

$$2BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + 2CO_2 \qquad (2)$$

Kubo and Shinriki [3–5] reported that orthotitanate could only occur by a reaction between $BaCO_3$ and $BaTiO_3$ according to the reaction,

$$BaCO_3 + BaTiO_3 \rightarrow Ba_2TiO_4 + CO_2. \qquad (3)$$

Ba_2TiO_4 was able to react subsequently with the remaining titanium oxide to reform the metatitanate

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3. \qquad (4)$$

In addition, the thermodynamic data relative to the various possible equilibria between $BaCO_3$, TiO_2, CO_2, $BaTiO_3$ and Ba_2TiO_4 were calculated by Kelley *et al.* [6]. These data enabled Templeton and Pask [7] to show that the formation of metatitanate, through barium oxide BaO which results from the carbonate decomposition, is not to be excluded to the extent that the partial pressure of the carbon dioxide in the reaction atmosphere is close to the dissociation pressure of $BaCO_3$.

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The same authors showed that the orthotitanate can only form through Reaction 3. Thermodynamic calculations showed that under one atmosphere of CO_2, the orthotitanate should occur at 760° C if the reaction takes place according to Reaction 2 and at 1100° C by Reaction 3; now experiments, notably those of Kubo *et al.* [8], confirmed the second alternative.

Finally, according to Cournil *et al.* [9, 10] the formation rate of $BaTiO_3$ by Reaction 1 was a decreasing function of the CO_2 or nitrogen pressure whereas the rate law against oxygen pressure plot at 720° C showed a minimum for 150 torr.

This research shows the close link between the presence of orthotitanate in the calcination product and the nature of the surrounding gas. This led us to analyse quantitatively the phases occurring during calcination carried out under different atmospheres: in air since industrial treatment is performed in this way, under vacuum to obviate the reaction atmosphere and finally under carbon dioxide pressure.

The present paper sums up the results of the various experiments.

2. Experimental details

A series of preliminary experiments was made to determine the choice of materials, the preparation conditions of the reaction mixtures and the calcining reaction properly.

The barium carbonate used was witherite of specific area 2 to $3\,m^2\,g^{-1}$; the titanium oxide was anatase of specific area 8 to $10\,m^2\,g^{-1}$. The oxide was used slightly in excess of that to form $BaTiO_3$ but the Ti/Ba ratio, however, remained less than 1.08 to prevent the formation of phases richer in titanium than $BaTiO_3$.

The $BaCO_3$ and TiO_2 mixture was made by performing a slip in a process comparable to that used in industrial production. The tests made on dry mixtures showed that, under the same calcination conditions, the amount of orthotitanate formed was more than the amount obtained from wet mixed products.

The calcining reaction was achieved in a Setaram microbalance (MTB 10–8) the furnace of which allowed temperatures as high as 1500° C to be reached. A 20 mg mixture, contained in a platinum crucible, was used in each experiment.

All the experiments were carried out in a similar way: the linear temperature rose up to 900° C (600° C h^{-1}), then this temperature was maintained for a period of time which varied from one experiment to another; this allowed for different extents of progress of the reaction. Finally the temperature was lowered rapidly to room temperature to quench the sample. The reaction mixture was then either qualitatively analysed by X-ray diffraction or by a method to which we will refer to later.

It should be noted that the temperature of 900° C, much less than the temperature of industrial calcination (1100 to 1200° C) was selected to facilitate thermogravimetric measurements. The preliminary experiments have shown that, over the range 750 to 1200° C, temperature only affects the reaction rate; it modifies neither the nature of the phases formed nor the chronology of their occurrence.

3. Results

3.1. Thermogravimetric study of calcination in air

Diffractometric analysis of a quenched mixture which had undergone, about 25% reduction, showed the presence of $BaTiO_3$ and of Ba_2TiO_4.

Now, as we have seen, the formation of Ba_2TiO_4 may result from two reactions, either by Reaction 2, which competes the synthesis of $BaTiO_3$ by Reaction 1, or by Reaction 3.

The thermogravimetric recording, whilst allowing measurement of the number n of moles of CO_2 released according to Reactions 1 and 2 or 1 and 3, does not allow an assessment of the proportions of each titanate. To determine these proportions after different extents of reaction of calcination we have transformed the orthotitanate formed by reacting it with CO_2 according to Reaction 5

$$Ba_2TiO_4 + CO_2 \rightarrow BaTiO_3 + BaCO_3 \qquad (5)$$

The experimental process was as follows: when the sample, after rapid quenching, was at room temperature, the carbon dioxide was introduced into the thermobalance and then the mixture was reheated to 600° C, i.e. a temperature much lower than the temperature of initial calcination. Reaction 5 occurred and a weight gain was noted. The number n' of CO_2 moles, thus regained, corresponds to the number of Ba_2TiO_4 moles present in the sample. Hence the amount of $BaTiO_3$ may be assessed; indeed it was verified that whatever the reaction according to which the orthotitanate forms, Reactions 2 or 3, the number of $BaTiO_3$

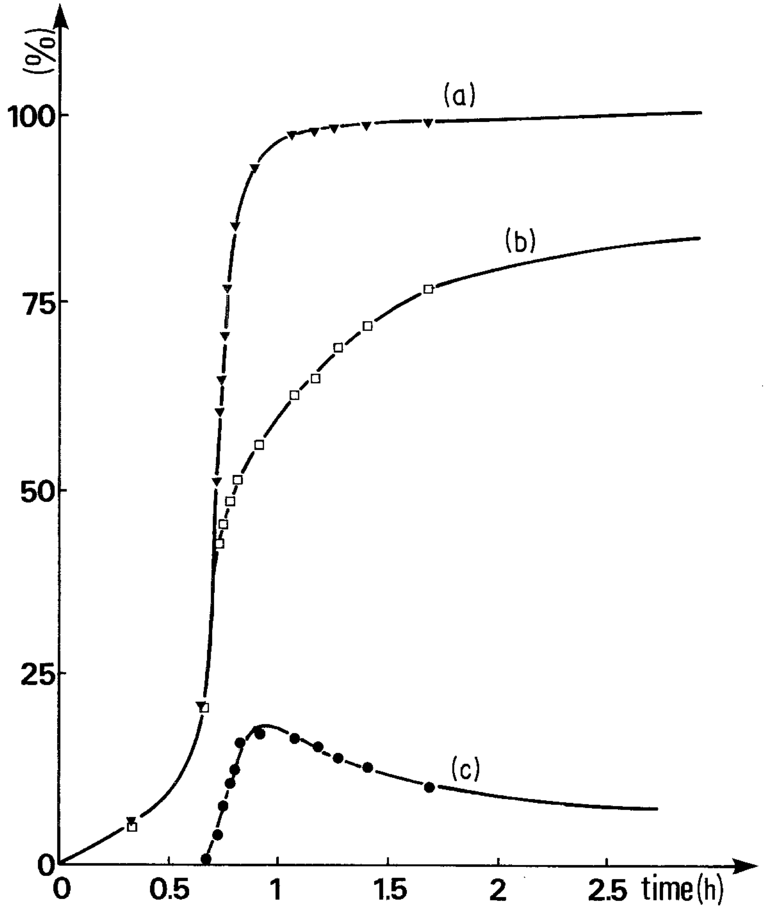

Figure 1 Variation of $BaTiO_3$ and Ba_2TiO_4% against time during calcination in air at 900° C (thermogravimetric study). (a) $\alpha = \Delta m/\Delta m_\infty \times 100$, (b) $x_1 = BaTiO_3\%$ and (c) $x_2 = Ba_2TiO_4\%$.

moles contained in the reaction mixture was given by the difference $n - 2n'$.

The percentages were calculated as follows

$$x_1 = \%BaTiO_3 = \frac{n - 2n'}{n_\infty} \times 100$$

$$x_2 = \%Ba_2TiO_4 = \frac{n'}{n_\infty} \times 100$$

where n_∞ is the total number of $BaTiO_3$ moles which would be formed by Reaction 1 alone going to completion.

Curve a in Fig. 1 shows the variation of the CO_2 loss against time at 900° C in static air. Curves b and c, respectively, show the variations of x_1 and x_2.

We noticed that in the early stages of the reaction, only $BaTiO_3$ forms. For a fraction reacted close to 25%, the orthotitanate begins to form – whereas the formation rate of $BaTiO_3$ is slowed down. The maximum extent of Ba_2TiO_4 was reached when the barium carbonate had completely disappeared from the reaction mixture, the latter being then only constituted by $BaTiO_3$, Ba_2TiO_4 and TiO_2, which was confirmed by the X-ray diffraction of the quenched samples.

The quasi total transformation of the initial mixture into $BaTiO_3$ was obtained after 30 h at the temperature of the experiment. The final stage of calcination was represented by the conversion of the orthotitanate probably due to the reaction with the remaining titanium oxide according to Reaction 4 [11].

X-ray diffraction analysis of the samples at different extents of calcination showed the occurrence, together with Ba_2TiO_4, of other phases in small amounts that could not be identified. They remained in the mixture obtained after treatment with carbon dioxide; their behaviour with respect to the latter is thus different from that of Ba_2TiO_4.

3.2. Thermogravimetric study of calcining under vacuum

The experimental process used for calcination in air was exactly reproduced in the experiments under a dynamic vacuum of about 10^{-3} torr. In the

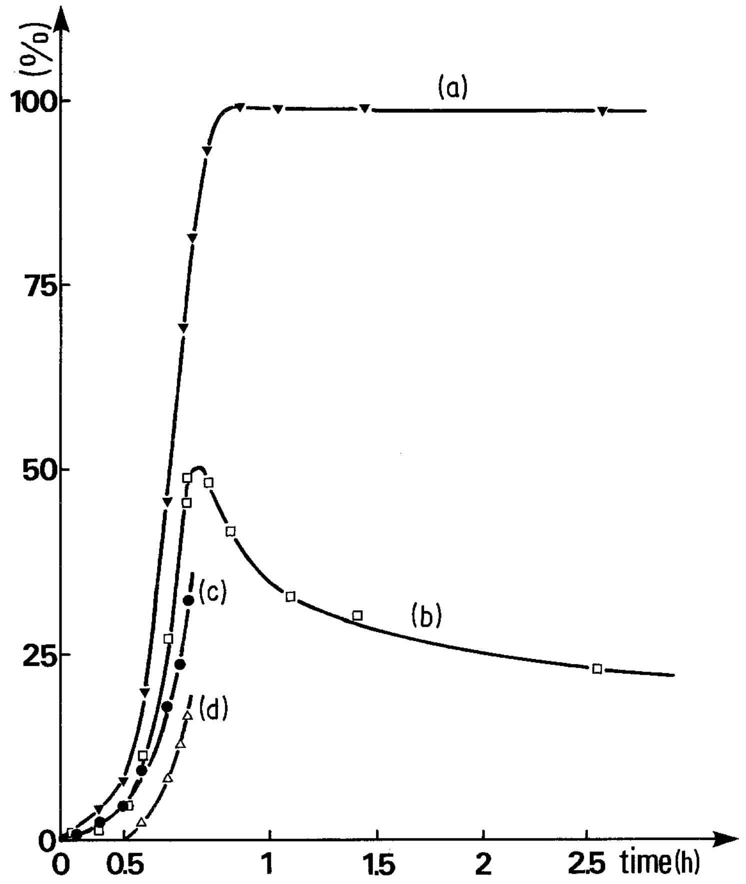

Figure 2 Variation in % against time of (a) weight loss during calcining under vacuum at 900° C, (b) weight gain during treatment under CO_2 at 600° C, (c) Ba_2TiO_4 % and (d) BaO%.

same way, the treatment by CO_2, of the reaction mixture obtained after quenching at different progress extents was carried out in the above-described conditions.

These experiments and the diffractometric analysis of the calcination product, quenched under vacuum showed a reaction process that is different from that observed in the air. Indeed:

1. Up to a fraction reacted of about 70% the reaction mixture contains orthotitanate Ba_2TiO_4 but no $BaTiO_3$
2. The weight gain recorded during treatment in CO_2 is greater than half of the CO_2 loss associated with calcination.

Now, whether Ba_2TiO_4 forms directly according to Reaction 2 or at the expense of $BaTiO_3$ through the two successive Reactions 1 and 3 the amount of CO_2 consumed by the transformation of Ba_2TiO_4 during Reaction 5 can only be equal to half the weight loss recorded during calcination. To explain these observations we must expect the formation, under vacuum, of another compound which in a CO_2 environment fixes the latter. The most probable reaction is the decomposition of barium carbonate

$$BaCO_3 \rightarrow BaO + CO_2 \qquad (6)$$

Although the barium oxide was not detected in the calcination product the barium orthotitanate and oxide are the only two phases whose occurrence releases CO_2. It is thus possible, from the measurements made during the two stages of thermogravimetric analysis, to deduce their proportion for different transformation extents of the intitial mixture.

The curves in Fig. 2 show the results obtained. The points on curve a correspond to the fractions reacted (in %) during calcination at which analyses were performed; curve b shows the weight gain recorded during treatment with CO_2 after obtaining the corresponding point of curve a; curves c and d, respectively, show the per cents of Ba_2TiO_4 and BaO in the reaction mixture. The descending part of curve b shows the progressive transformation of Ba_2TiO_4 into $BaTiO_3$ by reaction with the remaining titanium oxide, Reaction 4.

3.3. Thermogravimetric study of calcination under CO_2

The cycle of thermal treatment of the mixture $BaCO_3$ and TiO_2, consisting of a linear temperature rise up to 900° C, a temperature step then cooling down to room temperature linearly, was performed under a static atmosphere of CO_2 of about $10^5\,N\,m^{-2}$ (1 bar). Under these conditions, the reaction is largely slowed down; however, the weight loss still tends towards the loss of one CO_2 mole for one initial $BaCO_3$ mole; no weight gain was recorded during cooling.

Contrary to experiments performed in air or under vacuum, X-ray diffraction analysis of the samples at various stages of reaction showed the absence of orthotitanate Ba_2TiO_4 and the presence of another phase. The latter, like Ba_2TiO_4, occurred transiently in the synthesis of $BaTiO_3$ since, on the one hand, its occurrence is consecutive to that of $BaTiO_3$ and, on the other, its transformation at the end of calcination leads to metatitanate.

This intermediate phase is that already detected in very small amounts in the calcination product obtained in air and which could not be identified with any of the titanates known.

4. Discussion

The quantitative aspect of the experiments performed supplements the results already obtained on the synthesis of $BaTiO_3$. The observations made enabled us to identify the chemical process of occurrence and disappearance of the phases concerned, notably when heating was carried out in air or under vacuum.

4.1. Formation and transformation processes of $BaTiO_3$ and Ba_2TiO_4 during calcination in air

This process accounts for the transient occurrence of Ba_2TiO_4. The metatitanate $BaTiO_3$ occurs at the beginning of heating by the reaction between the barium carbonate grains and titanium oxide according to Reaction 1. The grain cores of the two precursors are separated, after some reaction time, by metatitanate which opposes the diffusion of barium towards TiO_2. The orthotitanate then forms at the expense of $BaTiO_3$ according to Reaction 3.

The orthotitanate might react with TiO_2 (although the two solids are not in contact) to yield the metatitanate according to Reaction 4. The rate of Reaction 3 would be higher than that of Reaction 4 which would explain the rapid increase of the Ba_2TiO_4 proportion in the sample. This is probably due to the localization of one to the other of the phases concerned in each reaction.

When all the $BaCO_3$ has disappeared, Reaction 3 stops and the final reaction is according to Reaction 4.

These observations exclude the direct formation of Ba_2TiO_4 by reaction between barium carbonate and titanium oxide and the assumption proposed conforms to the results obtained by Templeton and Pask [7], Kubo and co-workers [3–5, 8] and Yamaguchi *et al.* [11].

4.2. $BaTiO_3$ and Ba_2TiO_4 formation process during calcination under vacuum

In this case the reaction process must explain the presence, during initial heating, of only the orthotitanate and the existence in the reaction mixture of barium oxide BaO. Two schemes are possible.

First scheme

Heating yields three successive reactions

(a) decomposition of barium carbonate according to Reaction 6

(b) formation of Ba_2TiO_4 by reaction between the two oxides

$$2BaO + TiO_2 \rightarrow Ba_2TiO_4 \qquad (7)$$

(c) finally synthesis of metatitantate according to Reaction 4.

In this assumption the accumulation of Ba_2TiO_4 and BaO, so long as barium carbonate remains, could be explained by the fact that Reaction rates for Reactions 6 and 7 are higher than that of Reaction 4.

Second scheme

The formation of Ba_2TiO_4 is here consecutive to that of $BaTiO_3$. Four reactions are to be considered:

(a) decomposition of $BaCO_3$ according to Reaction 6

(b) formation of $BaTiO_3$ by direct reaction between the oxides

$$BaO + TiO_2 \rightarrow BaTiO_3 \qquad (8)$$

(c) formation of Ba_2TiO_4 at the expense of $BaTiO_3$ according to

$$BaO + BaTiO_3 \rightarrow Ba_2TiO_4 \qquad (9)$$

(d) formation at the end of calcination of $BaTiO_3$ according to Reaction 4.

As in the first scheme, the accumulation of Ba_2TiO_4 and BaO at the beginning of calcination and the occurrence of $BaTiO_3$ at a later stage can be explained only if Reactions 6 and 9 are rapid and Reactions 8 and 4 slow.

Experimental observations do not allow a choice of one of these schemes. In addition, Kelley *et al.*'s [6] thermodynamic calculations give no information about the titanate formation by reaction between the oxides.

We may, however, notice that the second model is close to that proposed to explain observations made during heating in air. This assumes that, in the absence of CO_2 (vacuum, flow of an $O_2 + N_2$ mixture), the metatitanate occurs first as in the case of calcining under low CO_2 pressure (in the air). The formation reaction of Ba_2TiO_4 at the expense of $BaTiO_3$ would be faster as the CO_2 pressure falls so that under vacuum it completely masks the occurrence of $BaTiO_3$ up to an extent of calcining close to 70%.

5. Conclusion

The above study is twofold.

(a) First, more fundamentally, it concerns a knowledge of the formation mechanism of different phases and will be developed in a further paper [12].

(b) Second, from an applied viewpoint, it shows the complexity of the chemical system during calcination, i.e. the transformations in solids and of the influence of the reaction environment; the formation process of $BaTiO_3$ is, alternatively, highly affected by the nature of the reaction atmosphere. Indeed, depending on its difference, intermediate compounds may occur. Nevertheless the system always tends towards a 100% composition of $BaTiO_3$ whatever the nature of the surrounding gas and whatever its pressure.

In the case of industrial calcination the atmosphere is rather complex, consisting of injected air and combustion gas from the burner. The CO_2 partial pressure is rather badly controlled. However the analysis of industrial calcines shows that the intermediate phase formed is Ba_2TiO_4. Taking our results into account it appears that two factors are to be considered. On the one hand an optimum partial pressure of CO_2 has to be maintained since, in an atmosphere poor in CO_2, the proportion of Ba_2TiO_4 may reach large proportions and in an atmosphere rich in CO_2 the orthotitanate is replaced by another phase whilst the formation rate of metatitanate is largely slowed down. On the other hand, the calcining time should be sufficient so as to allow the transformation according to Reaction 4 of the orthotitanate intermediately formed.

Acknowledgements

The authors wish to thank the CCM division of DGRST (Secrétariat d'Etat à la Recherche – République Française) for financial help as well as the LCCC–CICE division of THOMSON-C.S.F. for the grant to one of them (AB).

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Received 1 December 1982
and accepted 24 February 1983