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CONSTANT RATE THERMAL ANALYSIS (CRTA) AS A TOOL FOR THE SYNTHESIS OF MATERIALS WITH CONTROLLED TEXTURE AND STRUCTURE

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Abstract

Some examples of the use of the CRTA method for the synthesis of materials with controlled texture and structure are given. $BaTiO_3$ has been obtained from the thermal decomposition of Barium Titanyl Oxalate (BTO) and Barium Titanyl Citrate (BTC) by controlling the reaction temperature in such a way that the partial pressure of the gases generated in the reaction was maintained constant at a value close to 10^{-2} mbar. It has been shown that this method allows getting $BaTiO_3$ with crystal sizes considerably lower than those obtained by decomposing the same precursors by conventional methods. This small crystal sizes lead to the stabilisation of the metastable cubic phase with regards to the tetragonal phase.

It has been also shown that the control of the CO generated in the carbothermal reduction of silica allows tailoring the phase composition of the silicon nitride obtained as final product.

Keywords: CRTA, material synthesis

Introduction

The applications of the so-called structural materials are strongly dependent on the crystal size and their phase composition. The synthesis of nanosized $BaTiO_3$ is of great interest in order to diminish the synthesis temperature in the processing of multilayer capacitors [1–3]. The Barium Titanyl Oxalate (BTO) and the Barium Titanyl Citrate (BTC) obtained by coprecipitation according to the Pechini synthesis [4] have been used as precursors for barium titanate. However, the values of the crystal size of this material obtained from the thermal decomposition of these precursors seem to be considerably larger than those resulting from the hydrothermal synthesis or the thermal decomposition of alkoxides, that takes place at lower temperatures than that of the corresponding oxalates and citrates. It is noteworthy to point out that many publications [5–7] have been devoted to find new alternative ways for synthesising nanosized $BaTiO_3$. However, practically no effort has been dedicated to study the influence of the experimental conditions used for the thermal decomposition of the precursors on the morphology of the final products. To compare the microstructure of the $BaTiO_3$ obtained from the thermal decomposition of BTO and BTC by

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conventional methods and by controlling the thermal decomposition the CRTA method would be of interest. This technique has been successfully used for controlling the texture and structure of materials obtained from the thermal decomposition of the corresponding precursors [8–13].

It has been found that for the fabrication of Si_3N_4 ceramic bodies, it is advantageous to begin with α-Si_3N_4, because, although it transforms to the β phase modification when hot pressed, the final bodies have better mechanical properties than when manufactured directly from β-Si_3N_4 powders [14, 15]. Durham *et al.* [16] have concluded that the yields of Si_3N_4 from the carbothermal reduction of silica according to the reaction

$$SiO_{2(s)} + 6C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_4 + 6CO_{(g)} \qquad (1)$$

are strongly dependent on the partial pressure of CO, even in the range of low pressures that are very difficult to control, since CO is a reaction product. CRTA would be a proper tool for controlling the partial pressure of this gas along the experiment. Moreover, it would allow to determine if there is any relation between the partial pressure of CO and the α/β ratio in the phase composition of silicon nitride.

Experimental

$BaTiO(C_2O_4)_2 \cdot 4H_2O$ (BTO) was prepared by coprecipitation following the method described by Clabaugh *et al.* [17] using barium chloride dihydrate, titanium chloride and citric acid (Merck pro analysis) as starting materials. $BaTiO(C_6H_6O_7)_2 \cdot C_6H_8O_7 \cdot 7H_2O$ (BTC) was prepared in a similar way but using citric acid (Merck pro analysis) instead of oxalic acid.

The thermal decomposition of both BTO and BTC was carried out under vacuum by using the CRTA technique described elsewhere [10, 18]. A conventional vacuum apparatus equipped with a Pirani and Penning gauges interfaced to the sample heater through a PID temperature controller basically constitutes the experimental tool. The constant rate is attained both by controlling the residual pressure in the close vicinity of the sample and by maintaining a constant value of the pumping rate that can be selected by means of a vacuum leak valve. The constant decomposition rate, C, represents the fraction of solid reacted per minute. Thus, 1/C represents the time at which the decomposition of the oxalate is completed.

Silica gel and carbon from Aldrich have been used for the carbothermal synthesis of silicon nitride. The synthesis of Si_3N_4 has been carried out in a horizontal tubular furnace of high temperature (up to 1600°C). The sample constituted by a mixture C/SiO_2 in a molar ratio 2/1 was located into a graphite boat. A mixture of 95% nitrogen+5% hydrogen has been used both as reactive and carrier gas. A flow rate of 300 $cm^3\ min^{-1}$ has been used. The flowing gas sweeps the CO generated in the reaction through an IR sensor for carbon monoxide interfaced to the furnace temperature controller. The equipment allows monitoring the temperature of the furnace in such a way that the concentration of CO is maintained constant at any value previously selected by the user in the range from 100 ppm up to 2%. Moreover, the reaction rate at every particular concentration of CO can be chosen by properly selecting the nitrogen flow rate.

The powder diffraction diagrams were recorded with a D-500 Siemens powder X-ray diffraction system using CuK_α radiation.

The crystalline structure of $BaTiO_3$ has been assayed from the analysis of the symmetry of the (200) family of diffraction peaks [19]. The full-width of the half maximum (FWHM) of (111) diffraction peak has been used for calculating the medium diameter of the coherently diffracting domain according to the Scherrer equation. The tetragonality of the sample has been expressed by the value of the c/a ratio. The a and c lattice parameters were determined by processing all the XRD peaks recorded in the range from 20° to 90° (2θ) by means of the DISCVOL 91 computer program [20] assuming a tetragonal symmetry.

The α/β phase ratio in the Si_3N_4 obtained from the carbothermal reduction of silica has been estimated from the relative intensities of the (210) and (200) X-ray diffraction peaks of α-Si_3N_4 and β-Si_3N_4, respectively.

Results and discussion

It was reported in a previous paper [10] that the conventional synthesis of $BaTiO_3$ from the thermal decomposition of BTO under air atmosphere requires us to heat this precursor up to 750°C in order to complete the reaction. The textural and structural data of the $BaTiO_3$ here obtained from the thermal decomposition of BTO under air atmosphere at 750°C are summarised in Table 1. X-ray diffraction and TG confirmed that the decomposition of BTO was completed under these experimental conditions after 2 h at 750°C. It was tested, in a similar way, that the thermal decomposition of BCC was also completed after 2 h of heating at 750°C under air. The thermal treatment for all the $BaTiO_3$ samples here synthesised has been normalised by annealing for 2 h at this temperature, even for the samples obtained from CRTA experiments under vacuum, which show an important diminution of the decomposition temperature of BTO and BTC. The crystal size and the crystalline structure determined for the $BaTiO_3$ samples obtained under different experimental conditions are shown in Table 1. It can be observed that the samples obtained from CRTA experiments exhibit a medium crystal size considerably lower than the ones obtained from the thermal decomposition of the corresponding precursors under air. The very

Table 1 Textural and structural characteristics of the $BaTiO_3$ samples obtained from the thermal decomposition of BTO and BTC under vacuum (by means of the CRTA method) and open atmosphere, respectively

Sample	Procursor	Pressure	C/min^{-1}	$D_{\mathrm{scherrer}}/\mathrm{Å}$	Crystalline structure
1	BTO	open air (1 atm)	–	340	tetragonal
2	BTO	$2\cdot10^{-2}$ mbar	$3\cdot10^{-3}$	167	cubic
3	BTC	open air (1 atm)	–	280	tetragonal
4	BTC	10^{-2} mbar	$1.6\cdot10^{-3}$	131	cubic

small crystal sizes obtained by means of the CRTA method lead to a stabilisation of the meta-stable cubic phase of $BaTiO_3$ with regards to the tetragonal phase.

The stabilisation of the cubic structure has been checked from the analysis of the symmetry of the (200) XRD peak. Figure 1 shows, by way of example, both the observed (200) XRD profile of the sample 2 described in Table 1 and the difference between the experimental curve and that calculated by assuming a Pearson VII symmetric function, together with the R_p and R_W fitting parameters. These results point out that the (200) XRD profile of this sample is quite symmetric, which means that is not splitted to peaks (200) and (002) proper of the tetragonal phase.

The evolution of the structure and texture of sample 2 described in Table 1 has been followed by measuring the tetragonality of the sample and coherent diffraction domain size as a function of the annealing temperature. The tetragonality of the sample has been determined from the full XRD profile analysis as described in the Experimental section. The coherently diffracting domain sizes have been calculated from the FWHM of the (111) peak. This peak has been selected because it does not undergo a splitting as a consequence of the cubic → tetragonal phase transition. Figure 2 shows the plot of the *c/a* ratio and the crystallite size as a function of the annealing temperature. These results point out an increase of the tetragonality of $BaTiO_3$ by increasing its coherently diffracting domain. Moreover, a *c/a* ratio higher than unity is reached at D values around 250 Å, which means that the cubic lattice of $BaTiO_3$ would be stabilised at lower values of the crystal size. An analysis of the values reported in Table 1 for this parameter together with the found crystalline structure supports the above statement. These results allow to propose that the stabilisation of the cubic phase of $BaTiO_3$ depends on the coherently diffracting domain size rather than on the particle size as suggested by other authors [2, 3, 19].

To maintain by conventional methods a low CO partial pressure during the carbothermal reduction of silica according to Eq. (1) is a very difficult task provided that the above gas is self-generated in the reaction. Thus, to control the pressure of CO implies to control the rate of production of Si_3N_4. Therefore, CRTA would be a proper experimental method for this purpose. A set of Si_3N_4 samples have been obtained at a constant reaction rate $C=9\cdot10^{-4}$ min^{-1} but at different residual pressures of

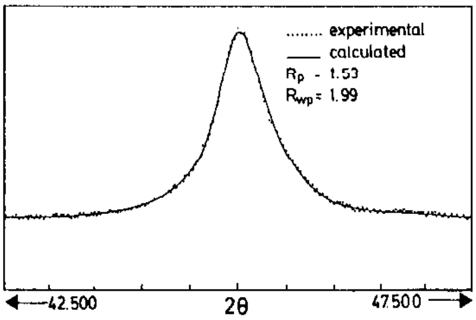

Fig. 1 XRD profile of the $BaTiO_3$ sample described in Table 1 and the final difference plot between the experimental curve and the curve calculated assuming a Pearson VII symmetric function

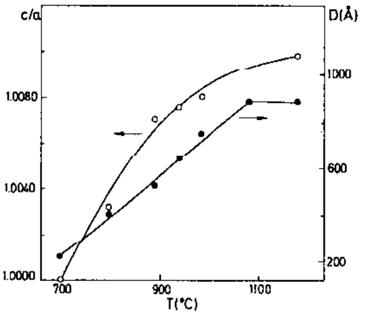

Fig. 2 Influence of the firing temperature of $BaTiO_3$ (sample 2) on both its tetragonality and its coherently diffracting domain size

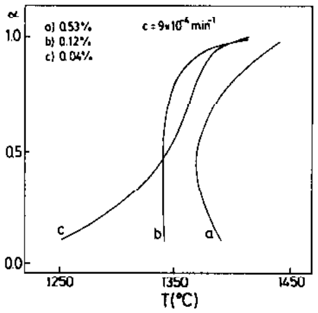

Fig. 3 α-*T* plots obtained at different concentration of CO and a constant reaction rate C–$9{\cdot}10^{-4}$ min^{-1}

CO that have been maintained constant all over the carbothermal process at values anging from 200 ppm to 0.53%. Figure 3 shows some of the α-*T* plots obtained in his way. The reaction was always completed, under these conditions, at temperaures lower than 1470°C. However, the reaction products were allowed to reach 1470°C and annealed for two hours at this temperature without interrupting the flow of 95% N_2+5% H_2 gas mixture. The reason for this standard thermal treatment for he whole series of Si_3N_4 samples was to make sure that their phase compositions, ncluded in Table 2, depend only on the experimental conditions used for the synthesis rather than on the final temperature reached by the sample.

The results included in Table 2 allow us to conclude that the concentration of α-Si_3N_4 phase in the products obtained from carbothermal reduction of silica dramatically increases by increasing the partial pressure of CO in the vicinity of the sample. On the other hand, the shape analysis of the CRTA traces [21] shows that, by increasng the CO concentration, at the time that the α-*T* profiles move at higher temperaures, the kinetics changes from being controlled either by a diffusion (0.04% CO) or phase-boundary process (0.12%) to obeying an Avrami-Erofeev mechanism when he CO concentration increases until 0.53%. Further research is necessary for clari-

Table 2 α-Si_3N_4/β-Si_3N_4 ratios for different CO concentrations at constant reaction rate $C = 9\cdot10^{-4}$ min^{-1}

CO/%	I_α/I_β
0.53	19.0
0.25	11.0
0.12	7.0
0.08	4.5
0.04	2.5
0.02	2.4

fying the mechanism of formation of α and β silicon nitride from carbothermal reduction of silica. However, the CRTA method has permitted by first time to establish the dependence between the formation of α-Si_3N_4 and the partial pressure of CO in contact with the sample.

In summary, the examples here outlined point out that the CRTA method could be a powerful tool for the synthesis of materials with controlled texture and structure.

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