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The new method of constant rate thermal analysis (CRTA): application to discrimination of the kinetic model of solid state reactions and the synthesis of materials [1]

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Abstract

The advantage of CRTA in discriminating the kinetics of solid state reactions by comparison with conventional non-isothermal methods is described. It is also shown that control of the thermal decomposition rate of $BaTiO(C_2O_4)_2 \cdot 4.5H_2O$ by CRTA gives $BaTiO_3$ with a particle size considerably smaller than that obtained by decomposing the mixed oxalate by conventional methods. The influence of the decomposition method of this compound on the crystalline structure of $BaTiO_3$ is analysed.

INTRODUCTION

The method of constant rate thermal analysis (CRTA) developed by Rouquerol [1–3] basically implies control of the temperature of a solid state reaction in such a way that its rate remains constant at a value previously selected by the user.

Application of CRTA in discriminating the kinetics of solid state reactions and controlling the texture and structure of $BaTiO_3$ obtained by thermal decomposition of the mixed oxalate is described in this paper.

RESULTS AND DISCUSSION

Discrimination of the kinetic model of solid state reactions

It is well known that the general expression of the reaction rate of a solid state reaction is

$$d\alpha/dt = Af(\alpha)\exp(-E/RT) \qquad (1)$$

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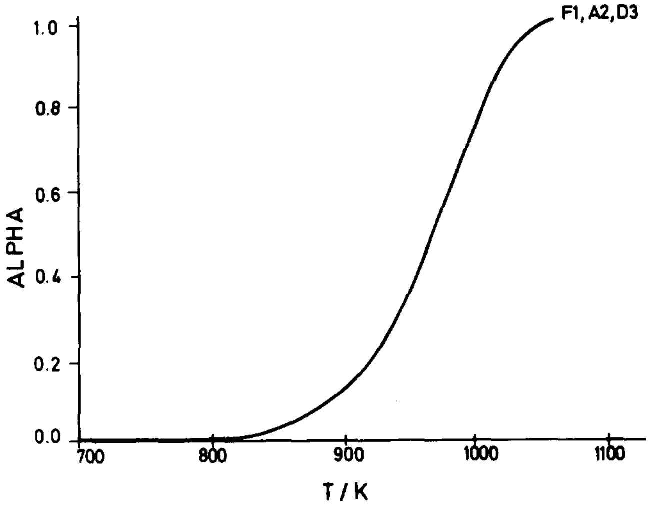

Fig. 1. A single TG curve for three kinetic models: F1 ($E = 167$ kJ mol^{-1}, $A = 1.6 \times 10^6$ s^{-1}), A2 ($E = 76$ kJ mol^{-1}, $A = 0.12 \times 10^2$ s^{-1}), D3 ($E = 308$ kJ mol^{-1}, A $= 6 \times 10^{12}$ s^{-1}).

where α is the molar extent of reaction. If a conventional TG plot is recorded at a linear heating rate $\beta = dT/dt$, eqn. (1) can be integrated by using the popular Coats and Redfern approach [4], and the following equation is obtained after rearranging in logarithmic form

$$\ln g(\alpha) - 2 \ln T = \ln AR/E\beta - E/RT \qquad (2)$$

where $g(\alpha)$ is a function depending on the reaction mechanism and the other parameters have their usual meaning.

It has been proved in previous work [5] that ln $g(\alpha)$ functions of the kinetic equations proposed in the literature for describing heterogeneous reactions are linearly correlated, and therefore that the actual reaction mechanism cannot be discriminated from a single TG trace. Figure 1 shows that a TG curve simulated by assuming a particular reaction mechanism is fitted by the other kinetic models, leading to different values of the activation energy and the Arrhenius exponential factor.

CRTA implies control of the temperature of the sample in such a way that the reaction rate remains constant; i.e., $d\alpha/dt = C$. Equation (1) can thus be written as

$$\ln 1/f(\alpha) = \ln A/C - E/RT \qquad (3)$$

It can be demonstrated that the ln $1/f(\alpha)$ functions corresponding to the different kinetic models of solid state reactions are not linearly correlated, and that the reaction mechanism can be discriminated from a single CRTA curve. This statement is proved in Fig. 2, which shows the theoretical curves calculated by assuming the kinetic models and parameters used for simulating the curve included in Fig. 1.

Application of CRTA to the synthesis of materials

CRTA provides effective control of the reaction rate and hence better efficiency in the control of heat and mass transfer phenomena than do conventional procedures. Rouquerol and Ganteaume [6] have shown that the particle size and porosity of Al_2O_3 obtained from the thermal decomposition of gibbsite can be tailored by selecting the appropriate decomposition rate. It has been therefore considered of interest to apply CRTA to obtain $BaTiO_3$ from the thermal decomposition of $BaTiO(C_2O_4) \cdot 4.5H_2O$ in order to compare its textural and structural properties with those obtained by thermal decomposition using a conventional method. Our experimental tool allows the constant decomposition rate C to be selected by controlling the residual pressure in the close vicinity of the sample and maintaining constant the value of the pumping rate of the vacuum system. This can be selected by means of a leak valve as described elsewhere [7].

Two samples have been prepared. Sample A was prepared by means of CRTA under a residual pressure of 2×10^{-2} mbar and a constant reaction rate $C = 3 \times 10^{-3}$ min^{-1} (i.e. the decomposition of the sample was completed in 330 min); the reaction was at 1043 K under the conditions described. Sample B was obtained by conventional decomposition of oxalate at 1073 K under air during 8 h.

The BET surfaces of samples A and B [8] are 14.4 and 4.3 m^2 g^{-1} respectively. If we assume spherical symmetry, we can estimate that their mean particle sizes are 0.03 μm and 0.12 μm. Thus, the particle size of the powder obtained by CRTA is considerably smaller. Moreover, sample A

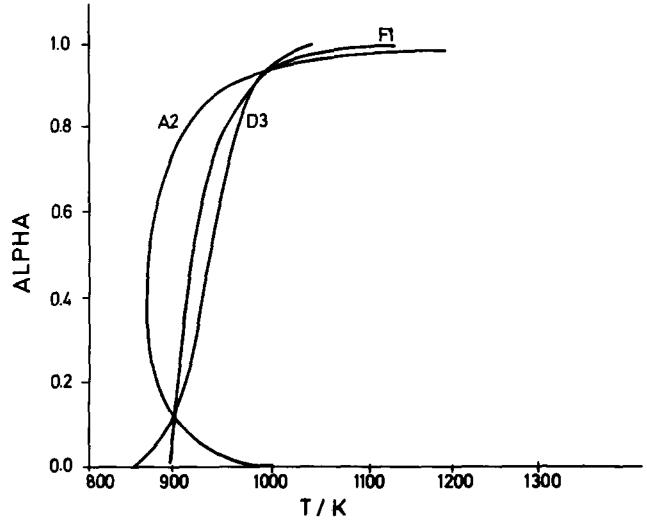

Fig. 2. Discrimination between the three kinetic models of Fig. 1 by means of the CRTA method; $C = 3 \times 10^{-4}$ s^{-1}.

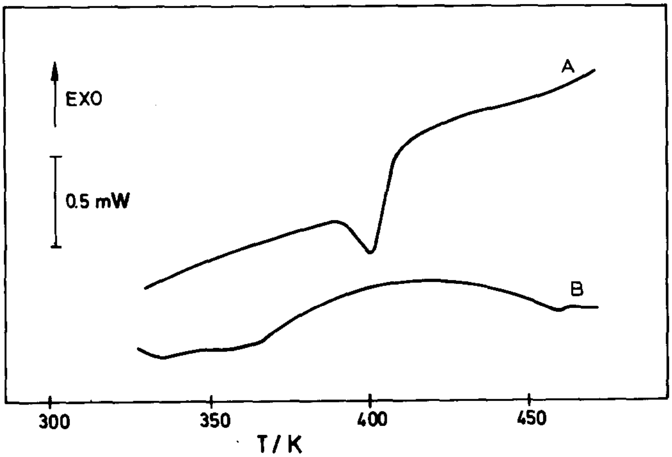

Fig. 3. DSC diagrams of samples A and B of $BaTiO_3$ recorded at a heating rate $\beta = 6$ K min^{-1}.

has a cubic structure, whereas sample B is tetragonal. The DSC curves of these specimens (Fig. 3) clearly show that sample A undergoes the ferroelectric–paraelectric phase transition at 398 K, whereas sample B does not.

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