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Resolution of overlapping peaks and the determination of kinetic parameters for the crystallization of multicomponent system from DTA or DSC curves: I. Non-isothermal kinetics

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Abstract

A new computer program has been created to separate overlapping exothermic and endothermic DTA (DSC) effects, obtained under non-isothermal conditions, occurring due to simultaneous nucleation and growth or more growth processes, and also to calculate the kinetic parameters of the processes represented by each peak.

A new graphical method for the initialization of the required parameters and the refinement of the initial values by the least squares method is presented.

The procedure for the determination of the kinetic parameters from DTA data is demonstrated on a model system and on a kinetic analysis of mullite formation from diphasic gel.

Keywords: Computer program; Crystallization kinetics; Differential thermal analysis; Mullite; Overlapping

1. Introduction

Simple, informative thermo-analytical techniques, including differential thermal analysis (DTA) and differential scanning calorimetry (DCS), are of particular importance in solid state phase transformation studies, especially in studies of crystallization in glasses and other amorphous materials.

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A large number of approaches have been formulated to analyse the experimental DTA or DSC data, all based on the formal theory of transformation kinetics [1-7]. The aim of them has been to generate a set of parameters from DTA (DSC) experiment that completely describes the kinetics of transformation and, when combined with other techniques such as microscopy and X-ray diffraction, provides an insight into the detailed mechanism of the transformation. Although often based on different and sometimes incorrect assumptions and approximations, they provide good results concerning isolated process [8]. However, certain glasses exhibit several stages of crystallization, affecting more compounds produced during the reaction, or a single compound with different stoichiometries. Therefore, the experimental registers obtained comprise two or more overlapping peaks. Also, if nucleation and growth take place simultaneously the thermal effects of nucleation and crystallization overlap. In this case conclusions reached for a single process are not applicable. There is an abscissa interval in which there are no experimental data concerning a single phenomenon; instead, the summed values of a number of simultaneous processes are available. If the overlap is small (the second process begins as the first is finishing) it can be ignored, but when the degree of overlap is high (nearly simultaneous processes) it is necessary to resolve the peaks. In order to solve the problem one must know the shape of the DTA (DSC) curve corresponding to a single crystallization process, i.e. the theoretical function associated with a single crystallization peak. Based on the assumed theoretical function, it becomes possible to resolve peaks and to discern the basic processes from which the overlapping DTA (DSC) data originate; this was the aim of this work.

2. Theoretical

The theoretical description of the progress of solid state transformations that involve nucleation and growth is represented by the formalism of Johnson-Mehl-Avrami [9-12] with the following relationship

$$\alpha(t) = 1 - \exp(-Kt^n) \tag{1}$$

This expression gives the fraction, α, of precursor that has been transformed into the product phase as a function of time, t; $K = k^n$ where k is the rate constant that reflects the rates of both nucleation and growth, and n is the Avrami exponent that reflects the details of the nucleation and growth mechanisms. The value of n depends on the reaction mechanism, growth dimension and nucleation rate and is usually shown by the equation

$$n = \frac{p}{s} + q = m + q \tag{2}$$

where p is the number of crystal growth dimensions ($p = 1, 2, 3$), s is a constant defining the limiting growth rate mechanism ($s = 1$ for phase boundary control and $s = 2$ for diffusion control) [13], q equals 0 for quenched nuclei, $0 < q < 1$ for retarded nucleation,

$q = 1$ for a constant nucleation rate and $q > 1$ for accelerated nucleation [14]. K and n are considered to be constants with respect to time. The Johnson–Mehl–Avrami equation has been found to describe accurately the transformations that occur in a wide variety of solid state processes is isothermal conditions. All of the analyses of thermo-analytical data from solid state transformations have employed this rate equation [1–7]. For most transformations, n is found to be constant over a substantial range of temperature. The rate constant, k, is a strong function of temperature, and this temperature dependence can be taken to be Arrhenian [15].

In calorimetric measurements of the solid state transformations, two basic methods can be used, isothermal and non-isothermal. Although the Johnson–Mehl–Avrami equation, in general, is not a valid description of transformations occuring under non-isothermal conditions, with certain assumptions and approximations it can be applied to data obtained by a non-isothermal method. The fact that the Johnson–Mehl–Avrami equation is a theoretical function that best adopts itself to experimental results obtained in both isothermal and non-isothermal processes has been proved by Surinach et al. [16].

Successful application of the thermo-analytical results to understand the process involved in transformations requires suitable methods for analysing the experimental data. The most common relations used to derive activation energy from the set of DTA (DSC) data, obtained by non-isothermal DTA (DSC) runs at different linear heating rates, were developed by Matusita et al. [5], Kissinger [6], and Augius and Bennet [7].

For the present purposes, the Matusita equation, Eq. (3), is taken as the basic function representing the integral function for transformation [5]

$$g(T) = -\ln(1-\alpha) = \frac{K}{\beta^n}\exp\left(-\frac{1.052nE}{RT}\right) \tag{3}$$

where α is the degree of crystallization, β is a linear heating rate, and n is known as the Avrami exponent. E is the overall effective activation energy for crystallization, $E = (mE_G + qE_N)/n$ [17], where E_G is the activation energy of growth and E_N is the activation energy of nucleation.

Eq. (3) can be written as

$$g(T) = \exp\left(\frac{a}{T} + b\right) = \exp\left(a\left(\frac{1}{T} - \frac{1}{T_p}\right)\right) \tag{4}$$

where $a = -(1.052nE)/R$, $b = \ln(K/\beta^n)$ and $1/T_p = -b/a$.

The appropriate differential function $f(T)$, according to Bezjak et al. [18], in this case is

$$f(T) = -ag(T)\frac{\exp(-g(T))}{T^2} \tag{5}$$

Once the mathematical function representing the shape of the experimental peak is found, the solution of the overlapping peaks is much easier. The experimental results, in the temperature interval where overlapping occurs, are the sum of those supplied by the overlapping processes. The relationship between the experimentally obtained DSC data denoted $F(T)$, and values corresponding to single a process is given by

$$F(T) = \sum_{i=1}^{N} w_i f_i(T) \tag{6}$$

where N is the number of overlapping peaks.

The object is now to find the number and species of peaks and then to establish the fraction and parameters corresponding to each individual process.

The first problem is to identify the overlap and to establish the number (N) and species of overlapping peaks. According to several authors [7, 15, 17, 19], in the case in which growth follows after nucleation the DTA (DSC) curve is asymmetrical, with the maximum corresponding to the maximum crystallization rate and to the amount of the crystallized fraction, α, equal to 0.63. Any deviation from this shape suggests retarded nucleation, or more than one growth process, or a diffusion-controlled crystal growth. As well as the shape of the curve being the first indication of overlapping, further information can be obtained by interrupting the DTA (DSC) experiment at various temperatures and submitting such samples to X-ray diffraction analysis. In this way, the order of crystallization is established. If there is only one crystalline phase, it is useful to observe the change in lattice parameters to indicate phase transformation. Very often a plot of $\ln(-\ln(1-\alpha))$ vs. $1/T$ is used to calculate the value of nE. In case of an individual DTA(DSC) peak, this plot is found to be linear and in the case of overlapping peaks, a break in linearity or an "s"-curve is seen. This break in slope can originate from the saturation of nucleation sites in the final stages of crystallization [20, 21] or from the restriction of crystal growth by the small size of the particles [22], or from the impingement of growing grains in the axial direction [23]; but very often it originates from overlapping. It must be pointed out that this break in slope is often neglected and the analysis is confined to the initial linear region; this approach is the case of overlapping peaks is obviously erroneous. Nevertheless, it can also be one of the overlapping indicators.

3. The computer model for resolving overlapping peaks in non-isothermal DTA and DSC

An algorithm based on Eqs. (5) and (6) can be developed into a program to resolve the overlapping DTA (DSC) peaks (superimposed because of two or more transformations in the same temperature interval) and to determine the kinetic parameters of the overlapping peaks. Therefore, in order to solve the problem of overlapping DSC peaks, the computer program OVERPEAK was created for separating overlapping peaks and for determining the process parameters corresponding to the individual peaks.

3.1. *Determination of the initial values of the parameters*

The usual method of initialization is to set the numerical values of the parameters once and to refine them instantaneously. The new graphical concept presented enables the direct selection of the number and species of the peaks and the indirect selection of the peak parameters by changing peak position and shape. Instead of an initialization of the peak parameters, the peaks themselves are initialized. The shape of the peak corresponds, of course, to certain combinations of parameters. The aim of such an initialization is to define the peaks obeying theoretical function(5) which correspond to the experimentally DTA (DSC) curve in segments where it most probably represents only one process. The curve obtained by adding up such maximum is then adapted in same manner to the shape of the experimentally obtained DTA (DSC) curves. Such a method enables corrections of the parameters before refinement and, consequently, a better initialization.

Three exothermic and one endothermic peaks can be initialized by choosing them from the menu bar. Once chosen, a peak appears with the following parameters: $T_p = T_p$ (experimental), $nE = 500\,\mathrm{kJ\,mol^{-1}}$, i.e. the corresponding values of a and b according to Eq. (5), and the value of w which depends on the number of peaks initialized and could be negative for an endothermic peak. Each parameter could be enlarged or reduced by pressing separate keys until the part of the initialized peak is adapted to the part of the experimental peak: with the enlarging of the nE value, the peak becomes narrower; the enlarging of the T_p value shifts the whole peak to higher temperatures; and on enlarging the w value, the peak becomes proportionally higher. By initialising the next peak, the sum curve appears. The aim is now to adopt the sum curve to the experimental curve, as much as possible, by changing the parameters of the initialized peaks. The number of peaks initialized and their positions have to be in agreement with the information obtained by interrupting the DTA (DSC) experiment at various temperatures, followed by X-ray diffraction analysis. The parameters initialized in such a manner are very close to real ones and permit successful refinement.

3.2. Refinement of the initial values of the parameters

It can be assumed that the interrelationship between $F(T)$ and the parameters a_i, b_i and w_i is

$$F(T) = \Phi(a_i, b_i, w_i) \tag{7}$$

Any change in a_i, b_i or w_i is reflected in the $F(T)$ function and thus the total differential of Eq. (7) reads [18]

$$\mathrm{d}F = \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{\delta F}{\delta p_{ij}} \mathrm{d}p_{ij} \tag{8}$$

where $p_i = a_i, b_i, w_i$, and N is the number of overlapping peaks.

After substitution of

$$\Delta F = F - F_c \tag{9}$$

(for $\mathrm{d}F$) and

$$\Delta p_{ij} = p_{ij} - p_{ijc} \tag{10}$$

(for $\mathrm{d}p_{ij}$) we obtain

$$\Delta F = \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{\delta F}{\delta p_{ij}} \Delta p_{ij} \tag{11}$$

where p_{ij} is the most probable value and p_{ijc} the initially calculated value or a value obtained from a lower refinement cycle. F denotes the experimentally determined value and F_c is the calculated value. The $\delta F/\delta p_{ij}$ expressions, where p_i is a_i, b_i and w_i respectively, are given by Eqs. (12), (13) and (14)

$$\frac{\delta F}{\delta a_i} = w_i f_i(T)(1 - g_i(T))\frac{1}{T} \tag{12}$$

$$\frac{\delta F}{\delta b_i} = w_i f_i(T)(1 - g_i(T)) \tag{13}$$

$$\frac{\delta F}{\delta w_i} = f_i(T) \tag{14}$$

The application of Eq. (11) to M experimental items of data gives a system of M equations with $3N$ unknowns, where $M > > 3N$. The best values for Δp_{ij} are obtained by the least squares method and the most reliable values for p_{ij} from Eq. (15)

$$p_{ij} = p_{ijc} + \Delta p_{ij} \tag{15}$$

The experimental curve was thus resolved into component parts, each representing an individual process with known kinetic parameters.

If the sum curve does not tend to adopt the shape of the experimentally obtained curve, the initialization should be repeated, most probably with different assumptions. The required number of refinement cycles depends on the system and the quality of initialization and is usually no larger than 20 cycles.

The program OVERPEAK is written in QB language ver. 4.5. The program uses ASCII files data obtained by on-line measurements, each representing one DTA or DSC curve. All results (separated peaks and calculated parameters) can be printed out or saved as an ASCII file.

3.3. Testing the program

In order to verify the validity of the program, it was tested on a model system of two overlapping exothermic peaks with the assumed parameters listed in Table 1.

The program has also been applied in the determination of the kinetic parameters of mullite formation from diphasic gel. Diphasic gel with a stoichiometric mullite composition was prepared by the coprecipitation method [24]. The kinetic parameters were determined by the non-isothermal method in a DTA apparatus (NETZSCH STA 409, air atmosphere, corundum as reference material).

4. Results and discussion

Fig. 1 and Table 1 show the results of applying the developed program to a model system. Very good agreement between simulated and calculated curves and between preset and calculated values of parameters is observed.

Table 1
Preset parameter values of the model system and the values of the model system calculated by the program

	1st peak		2nd peak	
	Preset	Calculated	Preset	Calculated
T_p/K	800	800	820	820
n	1		1	
E/kJ mol^{-1}	500		300	
nE/kJ mol^{-1}		502		295
w	0.67	0.66	0.33	0.34

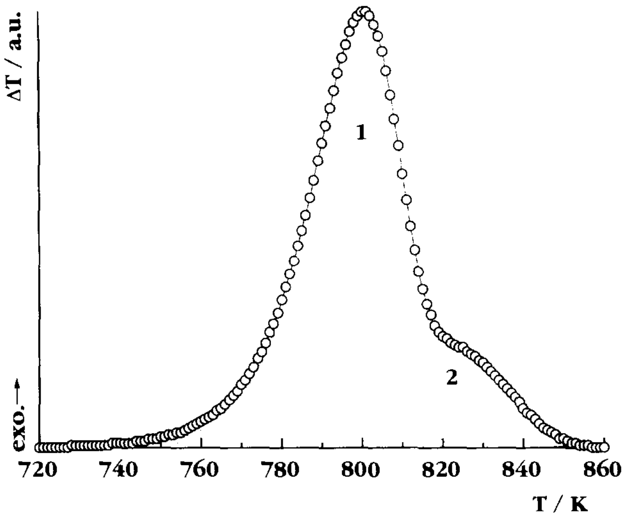

Fig. 1. Simulated DTA curve of the model system (o), separated peaks (---) and sum curve (–).

The program was also applied to studying the formation kinetics of mullite from the prepared diphasic gel. The DTA curve of the prepared gel shows two exothermic peaks (Fig. 2). The first, very small exotherm appearing around 1000°C is related to the crystallization of the Al–Si spinel phase [25,26], confirmed by XRD analysis (Fig. 3). The spinel remains stable until ~ 1280°C, and above this temperature it reacts with amorphous SiO_2 forming mullite (second exothermic peak in Fig. 2).

The second peak data, representing mullite formation, was submitted to analysis by the developed program. The first assumption was that mullite formation from Al–Si spinel and amorphous SiO_2 gives rise to a single exotherm on the DTA scan. The theoretical curve obtained under this assumption is inconsistent with the experimental one (Fig. 4). Therefore, the assumption of the existence of two overlapping exothermic peaks was made. The experimental DTA peak was resolved successfully, and satisfac-

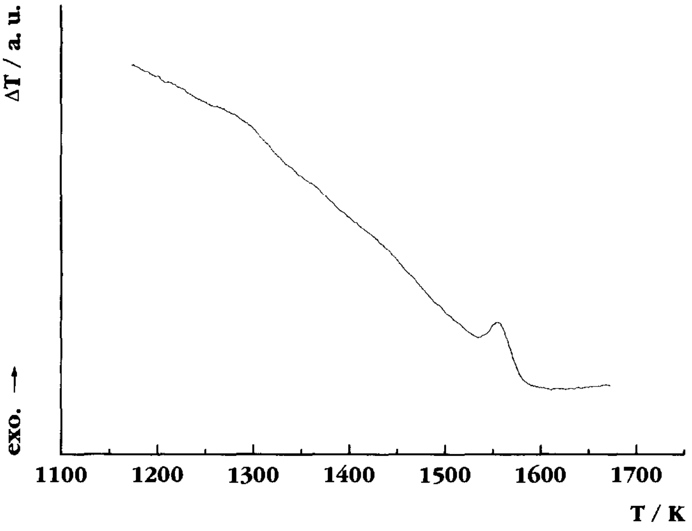

Fig. 2. DTA curve of the gel previously heat treated at 600°C for 2 h at the heating rate of 10°C min^{-1}.

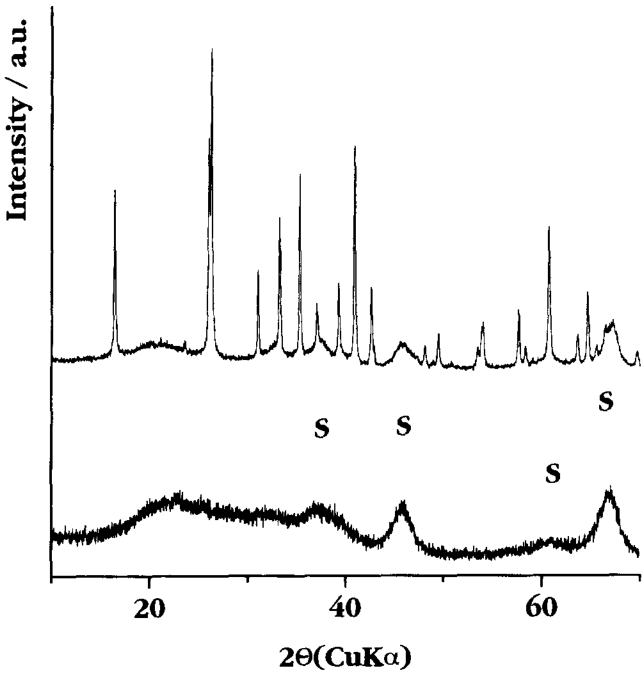

Fig. 3. Powder XRD patterns of the gel calcined for 2 h at various temperatures. S is spinel and the unmarked peaks belong to mullite.

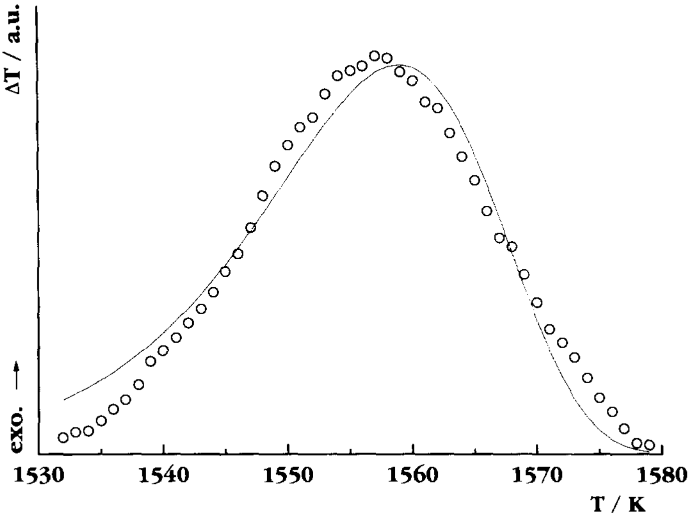

Fig. 4. Experimental DTA curve of the gel previously heat treated at 600°C for 2 h at the heating rate of 10°C min^{-1} (○) and corresponding theoretical single peak (—).

tory matching between experimental and calculated curves was obtained. Table 2 gives *nE* values of the resolved peaks calculated by the OVERPEAK program for DTA curves obtained at various heating rates (5, 7, 10, 15 and 20 K min^{-1}). The parameters denoted (1) correspond to the first peak and parameters denoted (2) correspond to the second peak. Fitting is illustrated (for one example) in Fig. 5.

Studying the isothermal mullite formation in diphasic gels by QXRD analysis, Ivanković et al. [27] have found that two different processes are involved in mullite

Table 2
Parameter values *nE*, T_p and *w* of the resolved peaks calculated by the developed program for DTA curves obtained at various heating rates; values of *E* obtained by applying Kissinger's equation and *n* values calculated from *nE* and *E*. The parameters denoted (1) correspond to the first peak and parameters denoted (2) correspond to the second

β/K min^{-1}	5	7	10	15	20
$T_p(1)$/K	1541	1549	1555	1563	1571
$nE(1)$/kJ mol^{-1}	3592	3164	2731	2452	2429
$w(1)$	0.39	0.41	0.46	0.49	0.53
$E(1)$/kJ mol^{-1}			933 ± 44		
$n(1)$	3.85	3.39	2.93	2.63	2.60
$T_p(2)$/K	1550	1557	1564	1573	1583
$nE(2)$/kJ mol^{-1}	3065	2745	2328	2014	1836
$w(2)$	0.61	0.59	0.54	0.51	0.47
$E(2)$/kJ mol^{-1}			847 ± 55		
$n(2)$	3.62	3.24	2.75	2.38	2.17

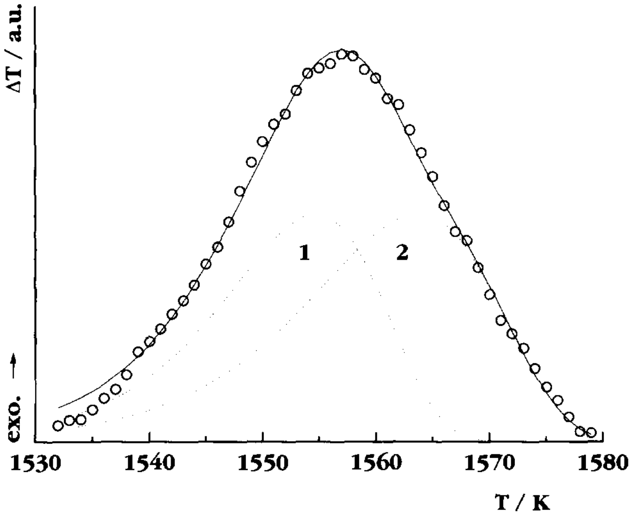

Fig. 5. Experimental DTA curve of the gel previously heat treated at 600°C for 2 h at the heating rate of 10°C min^{-1} (○), separated peaks (---) and sum curve (—).

formation. The first process to the nucleation and growth of metastable 2/1 mullite, and the second to its transformation into 3/2 mullite. Values of the parameter *a*, determined by XRD analysis using the least square method with silicon as standard, and the Al_2O_3 content in mullite, calculated from Cameron's plot [28], with respect to the quenched temperature, are given in Fig. 6. As there is no significant difference between the lattice parameter *a* of mullite in the temperature range 1265–1300°C, no transformation of 2/1 to 3/2 mullite is involved in the second exotherm. According to Schneider et al. [29], the transformation of 2/1 mullite to 3/2 mullite is a gradual process with no measurable enthalpy effect. Moreover, such a transformation would be diffusion-controlled [30] and it would not be correct to apply the function derived from the Johnson–Mehl–Avrami equation to describe it. Therefore, the appearance of two superimposed peaks is most likely due to unsimultaneous crystallization resulting from the different degrees of homogeneity of powders obtained by the precipitation technique. In parts with a higher degree of inhomogeneity, the crystallization is delayed.

Two independent linear functions $\ln(\beta/T_p^2)$ vs. $1/T_p$ were calculated [6], giving $E(1)$ and $E(2)$ values (Fig. 7). The values for $E(1)$, 933 ± 44 kJ mol^{-1}, and $E(2)$, 847 ± 55 kJ mol^{-1}, can be determined from the slope. These similar values indicate that both curves concern the same crystallization process. The obtained apparent activation energies are in good agreement with the values given in the literature [23, 30, 31].

The Avrami exponents were calculated by dividing the nE values obtained by the OVERPEAK program by the apparent activation energies obtained from Kissinger's [6] plot (Table 2). Differences in the nE values depending on β were observed. A decrease in nE, and in fact a decrease of the Avrami exponent with increasing heating rate, was observed in many other systems. An explanation for this phenomenon is found in the

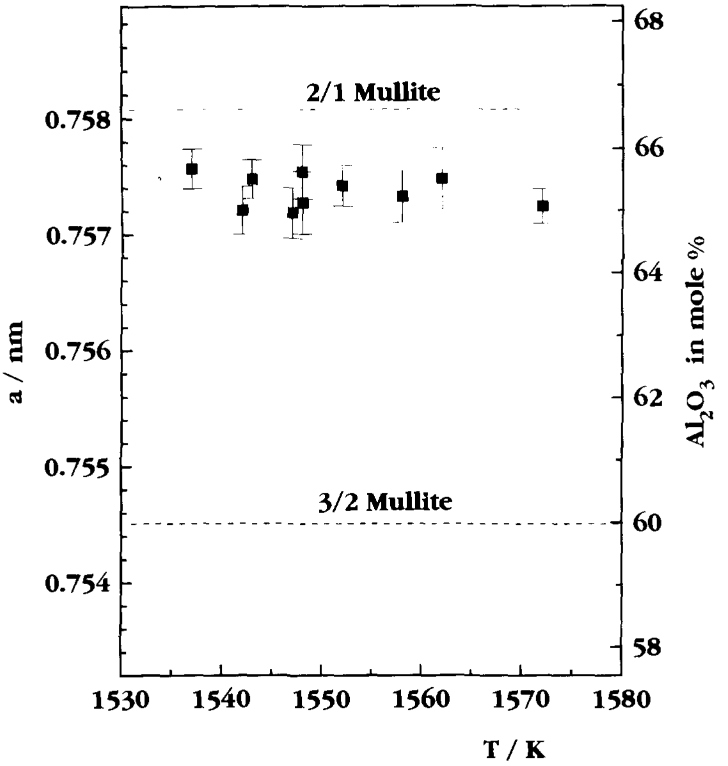

Fig. 6. Value of lattice parameter *a* and Al_2O_3 content in mullite with respect to the quenched temperature

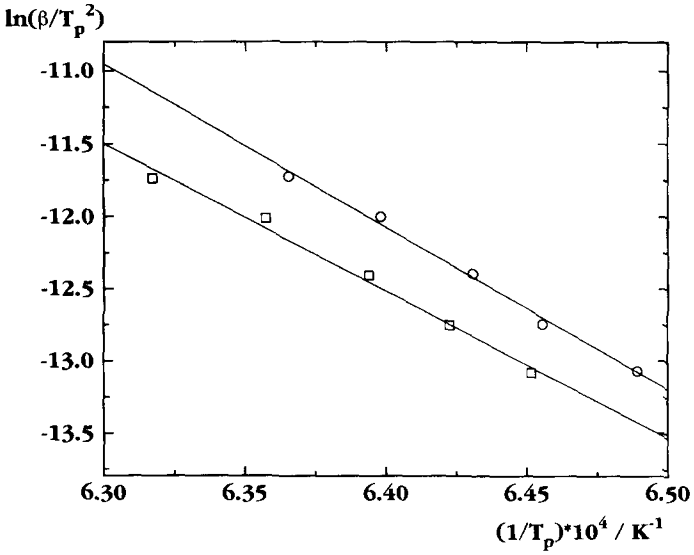

Fig. 7. Kissinger plots for resolved peaks: ○, first peak; □, second peak.

increasing contribution of surface crystallization with increasing heating rate [32]. With increasing β values, the n values decrease, in accordance with the change in nE values. The mean n values obtained are 3.1 and 2.8, which are also very similar values. In the literature [23, 30, 31], different values of the exponent n, from 1.3 up to 3.5, can be found for mullite crystallization from diphasic gels.

5. Conclusions

A new computer program OVERPEAK for separating overlapping DTA (DSC) peaks has been created. From such separated peaks, the kinetic parameters of processes represented by each peak can be calculated.

The program was tested on a model system consisting of two peaks with a high degree of overlap. A very good match between the simulated and calculated curves was obtained. The program was also tested on DTA scans of mullite crystallization from precipitated gels. Although one exotherm was observed on DTA scans representing mullite crystallization, it was shown that the exotherm has to be resolved into two separated peaks with different positions. The activation energies for the process of growth of 2/1 mullite are calculated to be 933 ± 44 and 847 ± 55 kJ mol^{-1} respectively, in good agreement with literature values. There is no significant difference in the apparent activation energies and Avrami exponents calculated on the basis of two separated peaks. Furthermore, the lattice parameter a observed in the peak temperature range was nearly constant. Therefore, the existence of two superimposed exothermic peaks must be attributed to a delay in mullite crystallization originating in a high degree of inhomogeneity in the mullite precursors.

Applying the OVERPEAK program to DTA or DSC data can only be successful if the proposed mathematical model corresponds to the kinetic process.

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