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NON-ISOTHERMAL KINETIC STUDY ON THE DECOMPOSITION OF Zn ACETATE-BASED SOL–GEL PRECURSOR

Part 1. Application of the isoconversional methods

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The isoconversional methods (Friedman (FR), Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS)) were applied for evaluating the dependencies of the activation energy (E) on the mass loss (Δm) corresponding to the non-isothermal decomposition of two Zn acetate-based gel precursors for ZnO thin films whose preparation differs by the drying temperature of the liquid sol-precursor (125°C for sample A, and 150°C for sample B). Although both investigated samples exhibit similar decomposition steps, strong differences between E *vs*. Δm curves as well as among the characteristic parameters of the decomposition steps, directly evaluated from TG, DTG and DTA curves, were put in evidence.

Keywords: *isoconversional kinetic methods, sol–gel, TG-DTG-DTA, thermal decomposition, Zn acetate-based precursor*

Introduction

Sol–gel method is very suitable and widely used for the preparation of zinc oxide-based nanoparticles [1–3], nanorods [4] and thin films [5–16] with advanced applications in optoelectronics, microelectronics, solar cells, etc. Two principal sol–gel routes to obtain oxide thin films are used: alkoxide route [5, 13] using organo-metallic precursors (often expensive and dangerous) and non-alkoxide route using water or alcohol solutions of metal salts such as acetates [1–3, 8–17] or nitrates [6, 7]. To obtain transparent and conductive ZnO-based thin films, the non-alkoxide route based on Zn acetate raw material has been used most frequently.

The sol chemical equilibrium, the substrate-film interaction during film deposition and the thermal processing of the as-deposited gel film (pre-heat treatment for film stabilization and post-heat treatment for film crystallization) contribute for the development of a particular film microstructure and subsequently particular electrical and optical properties [5, 13–16]. The chemical transformations associated with the decomposition of the gel precursor during the pre-heat treatment are decisive for the crystallization behaviour and the crystalline structure and properties of the final oxide films [5, 17–20].

In a previous paper [21], we presented the results on the thermoreactivity of zinc acetate based sol–gel precursor for ZnO thin films, in the temperature range 20–600şC, obtained by TG-DTA, IR and XRD methods. We have found that, from the sol–gel precursor containing $Zn(CH_3COO)_2{\cdot}2H_2O$ dissolved in 2-methoxyethanol in the presence of monoethanolamine (MEA) as complexing agent, ZnO is generated by heating in air above 150şC. The crystalline structure of the precursor heated in air at 200şC for 8 h is well defined in terms of ZnO hexagonal lattice parameters, although residual organic compounds and water were not yet fully removed. Increasing the treatment temperature up to 300, 400 and 600şC leads to a total decomposition and removal of the residual organic compounds and therefore to changes of the ZnO crystalline structure in terms of lattice parameters and grain size.

Although a large number of works on sol–gel preparation and properties of ZnO-based materials have been reported, less papers about thermal decomposition of precursors and no papers about the calculation of the kinetic parameters of precursors decomposition have been found. This paper presents the results, based on TG-DTG-DTA data, of a non-isothermal kinetic study concerning the thermal decomposition (between 150–250°C) of Zn acetate-based gel precursor obtained by drying the above mentioned liquid sol ($Zn(CH_3COO)_2{\cdot}2H_2O$ and $AlCl_3{\cdot}6H_2O$ dissolved in 2-methoxyethanol and MEA) at different temperatures. Differential and integral model-free (isoconversional) methods have been used [22, 23].

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Experimental

The preparation of liquid sol-precursor is presented elsewhere [21]. The solid samples for the kinetic study have been prepared by drying/heating the liquid sol in air for 8 h at 125 or 150°C (samples A and B, respectively). The choice of these temperatures was performed by observing the TG-DTG-DTA curves of the gel obtained by drying the liquid sol in air at 100°C [21].

TG-DTG-DTA data were obtained in flowing N_2 atmosphere (flow rate of 100 mL min^{-1}) at different heating rates (2.5, 5.0 and 7.5 K min^{-1}) using a LINSEIS STA PT1600 equipment.

The model-free (isoconversional) methods used to evaluate the activation energy

Friedman method [24] (FR method)

The differential isoconversional method suggested by Friedman (FR method) is based on the following equation:

$$\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\ln A+\ln f(\alpha)-\frac{E}{RT} \tag{1}$$

where α is the degree of conversion, T is the absolute temperature, β is the linear heating rate ($\beta=\mathrm{d}T/\mathrm{d}t=$ const., t is the time), A is the pre-exponential factor, E is the activation energy, $f(\alpha)$ is the differential function of conversion and R is the gas constant. For a given values of α, the plot $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)]$ *vs.* $1/T$, obtained from curves recorded at several heating rates, should be a straight line whose slope allows to evaluate the activation energy.

Flynn–Wall–Ozawa method [25, 26] (FWO method)

The isoconversional integral method suggested independently by Flynn, Wall and Ozawa uses Doyle's approximation [27] of the temperature integral. This method is based on the equation:

$$\ln\beta=\ln\frac{AE}{Rg(\alpha)}-5.331-1.052\frac{E}{RT} \tag{2}$$

where

$$g(\alpha)=\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}$$

is the integral conversion function. Thus, for α=const., the plot $\ln\beta$ *vs.* $1/T$, obtained from curves recorded at several heating rates, should be a straight line whose slope allows evaluating the activation energy.

Kissinger–Akahira–Sunose method [28] (KAS method)

This isoconversional integral method is based on the Coats–Redfern approximation [29] of the temperature integral. It was shown that [28]:

$$\ln\frac{\beta}{T^2}=\ln\frac{AR}{Eg(\alpha)}-\frac{E}{RT} \tag{3}$$

Thus, for α=const., the plot $\ln(\beta/T^2)$ *vs.* $1/T$, obtained from curves recorded at several heating rates, should be a straight line whose slope can be used to evaluate the activation energy.

Results and discussion

Non-isothermal decomposition of sol–gel precursor

As expected, the thermal decomposition of the sol–gel precursor is a rather complicated process especially due to the various kinds of organic molecules which are present.

Figures 1 and 2 show the TG-DTG-DTA curves, recorded in dynamic N_2 atmosphere at various heating rates, for samples prepared by heating the liquid sol at 125 and 150°C, respectively (samples A and B). The inspection of these curves shows that three endothermic steps occur at the progressive heating of both samples. The main parameters of these steps are listed in Tables 1 and 2. In a previous work [21], we suggested that step I corresponds to the water and 2-methoxyethanol losses, step II corresponds to the decomposition of zinc acetate and formation of an intermediary compound and that step III corresponds to the final decomposition of the intermediate compound formed in step II and to the decomposition of a rather stable Zn–MEA existing in the precursor [6, 10].

Comparing the thermal decomposition data of the mentioned samples (Tables 1 and 2), it can be noticed that the most significant difference is related to the step II, concerning the values of $T_{\max}$, T_f and $\overline{Dm_\mathrm{t}}$. For sample obtained at 150°C (sample B), the second step of decomposition is characterized by lower $T_{\max}$, T_f and $\overline{Dm_\mathrm{t}}$ values. A lower $\overline{\Delta m_\mathrm{t}}$ value was expected taking into consideration that in a previous paper [21] we showed that an important amount of zinc acetate precursor decomposed during the preparation of the sample B, by heating the liquid sol at 150°C. Lower $T_{\max}$ and T_f values could mean that ZnO crystallites generated during heating in air at 150°C act as catalyst for the decomposition of the precursor.

Dependence of the activation energy on the mass loss

The activation energy for a certain mass loss step was evaluated from the straight line slope of the corre-

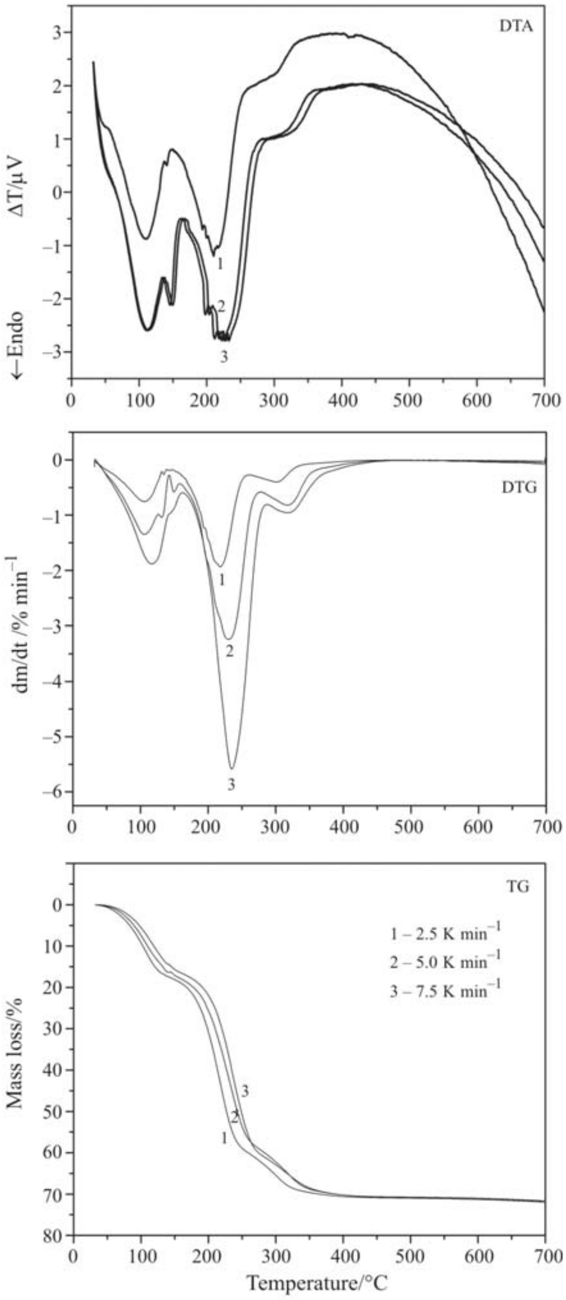

Fig. 1 TG-DTG-DTA curves for sample A, recorded in dynamic N_2 atmosphere at various heating rates for 1 – 2.5, 2 – 5.0 and 3 – 7.5 K min^{-1}

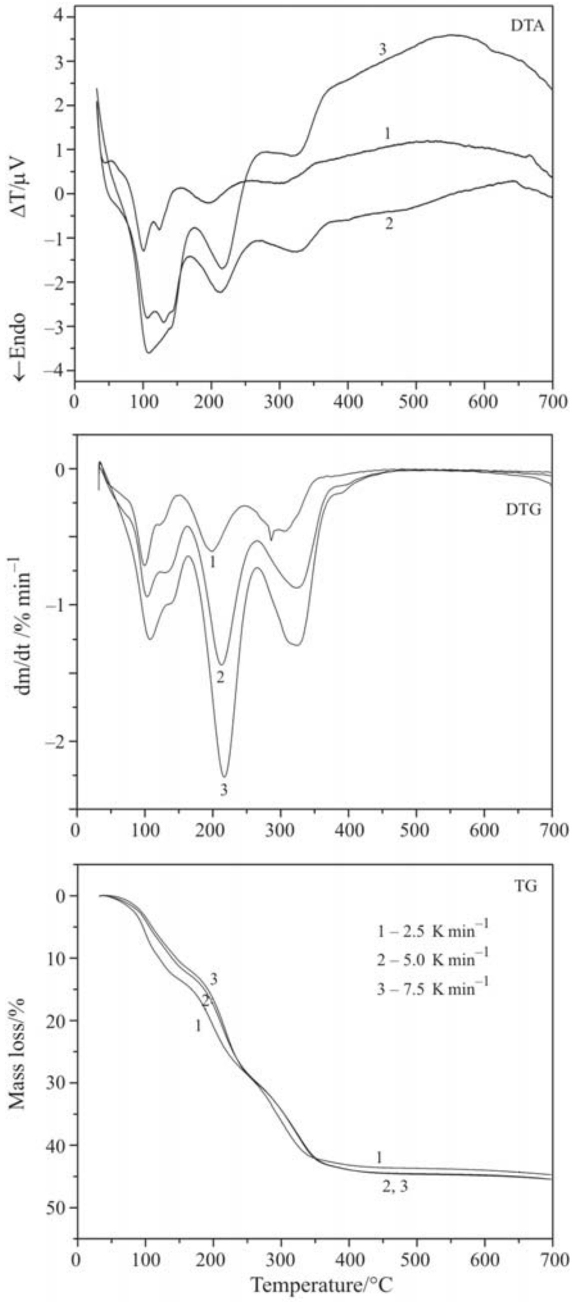

Fig. 2 TG-DTG-DTA curves for sample B, recorded in dynamic N_2 atmosphere at various heating rates: 1 – 2.5, 2 – 5.0 and 3 – 7.5 K min^{-1}

spondent FR, FWO and KAS isoconversional methods. It was considered that the *E* value is heating rate independent if the relative error of the slope of FR, FWO and KAS straight lines is lower than 10%. The obtained results are shown in Figs 3 and 4.

For sample A, prepared at 125°C, *E* values are heating rate independent only for the second step process (Fig. 3). For this mass loss step, *E* values calculated by the three isoconversional methods are in good agreement and are practically independent on the degree of conversion ($\overline{E}_{FR}$=100.2±3.7 kJ mol^{-1}, $\overline{E}_{FWO}$=97.7±2.8 kJ mol^{-1} and $\overline{E}_{KAS}$=94.7±2.8 kJ mol^{-1}). These values are close to that obtained by the use of the Kissinger method [30], applied to the DTA maxima (E_K=97.8±2.4 kJ mol^{-1}) [31].

A different dependence of the activation energy on the mass loss was obtained for the case of sample B, prepared at 150°C, (Fig. 4). First of all, a strong dependence of *E* values on mass loss was observed. *E* values determined by means of integral isoconversional methods (E_{FWO} and E_{KAS}) are in good agreement, but they are different from that determined by

Table 1 The parameters of the decomposition steps for sample A dried at 125°C

Step	β	Data from TG-DTG curves						Data from TG-DTA curves					
		T_i/°C	T_f/°C	Δm_t/%	$\overline{Dm_t}$/%	T_{max}/°C	m_{max}/%	T_i/°C	T_f/°C	Δm_t/%	$\overline{Dm_t}$/%	T_{max}/°C	m_{max}/%
I	2.5	32.3	141.5	17.7	16.9	106.0	10.95	32.3	148.8	18.0	17.8	111.1	12.5
	5.0	32.3	158.5	17.8		106.0	8.95	32.3	161.3	18.1		111.6	10.5
	7.5	31.9	161.3	16.6		116.6	9.4	31.9	168.6	17.2		123.0	11.0
II	2.5	141.5	259.3	42.3	42.8	218.0	25.6	148.8	260.8	42.2	42.6	210.4	19.7
	5.0	158.5	276.5	41.4		230.9	24.2	161.3	280.6	41.6		226.6	21.6
	7.5	161.3	286.6	44.8		234.7	23.5	168.6	284.1	43.9		234.5	22.7
III	2.5	259.3	–	11.9	11.3	301.0	5.6	260.8	–	11.8	11.6	301.0	5.4
	5.0	276.5	–	12.4		317.2	5.7	280.6	–	12.0		318.3	5.4
	7.5	286.6	–	10.3		317.6	3.7	284.1	–	11.1		320.9	–

β – heating rate in K min^{-1}; T_i and T_f – temperatures at the beginning and at the end of each decomposition step, according to DTG or DTA curves, respectively; T_{max} – temperature corresponding to maximum in DTG curve or minimum in DTA curve; Δm_t – total mass loss corresponding to each step; m_{max} – total mass loss from the beginning of heating until the maximum rate of the decomposition step

Table 2 The parameters of the decomposition steps for sample B dried at 150°C (the meaning of the notations is the same as in Table 1)

Step	β	Data from TG-DTG curves						Data from TG-DTA curves					
		T_i/°C	T_f/°C	Δm_t/%	$\overline{Dm_t}$/%	T_{max}/°C	m_{max}/%	T_i/°C	T_f/°C	Δm_t/%	$\overline{Dm_t}$/%	T_{max}/°C	m_{max}/%
I	2.5	32.4	145.7	13.4	12.3	98.6	5.8	32.4	148.8	13.6	13.1	99.46	6.1
	5.0	33.7	150.5	11.8		101.5	4.5	32.7	163.5	12.9		104.7	5.1
	7.5	32.2	163.5	11.8		107.9	4.7	32.2	177.2	13.0		107.8	4.7
II	2.5	145.7	239.5	14.9	17.4	193.5	7.3	148.8	242.3	15.1	16.7	191.4	6.51
	5.0	150.5	256.6	18.2		206.5	9.0	163.5	260.2	17.5		206.8	8.0
	7.5	163.5	265.1	18.4		217.0	9.5	177.2	269.2	17.6		215.6	7.9
III	2.5	239.5	348.8	14.1	13.7	297.5	8.9	242.3	344.5	13.6	13.3	295.3	8.3
	5.0	256.6	371.3	13.5		317.2	7.9	260.2	369.9	13.1		314.8	8.0
	7.5	265.1	383.8	13.4		324.4	8.2	269.2	384.3	13.0		327.6	8.4

Friedman differential method (E_{FR}). It has been shown that the existence of significant differences between E_{FR} and E calculated using all integral isoconversional methods are due to the way of deriving the relations, which ground the integral methods. These relations are derived considering that the activation parameters do not depend on the conversion degree. Obviously, if E and A depend on the conversion degree, these derivations are not correct. Therefore, in such cases, the FR method, which uses directly the equation of reaction rate, is recommended [32, 33]. From Fig. 4, for the three decomposition steps of sample B, the following dependencies of E_{FR} on Δm can be observed:

- for step I, E_{FR} decreases from 110.6 kJ mol^{-1} (for Δm=2%) to 29.9 kJ mol^{-1} (for Δm=11%);
- for step II, E_{FR} increases from 83.6 kJ mol^{-1} (for Δm=14%) to 166.4 kJ mol^{-1} (for Δm=24%);

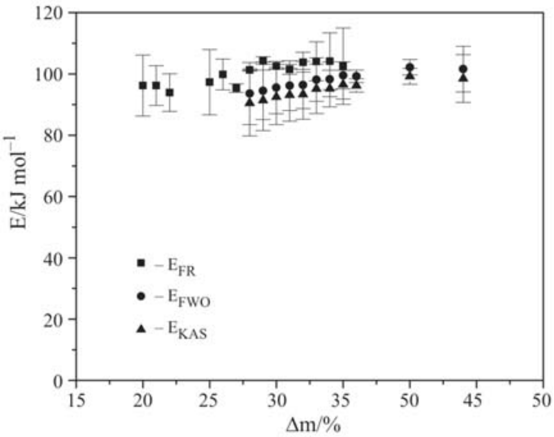

Fig. 3 *E vs*. Δ*m* for the second decomposition step of sample A

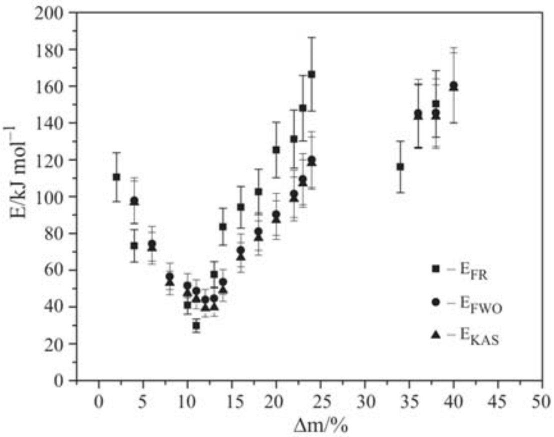

Fig. 4 *E vs*. Δ*m* for decomposition of sample B

- for step III, E_{FR} increases from 116.1 kJ mol^{-1} (for Δm=34%) to 150.4 kJ mol^{-1} (for Δm=38%).

This strong mass loss dependence of *E* values shows that all the decomposition steps of sample B exibit complex mechanisms.

Conclusions

The non-isothermal decompositions of two Zn acetate-based sol–gel precursors for ZnO thin films, whose preparation differs by the drying temperature (125°C for sample A and 150°C for sample B) were investigated by the thermal analysis methods (TG, DTG, DTA). It was pointed out that both samples exhibit three decomposition steps characterized by some specific parameters.

The evaluation, by means of the isoconversional methods (FR, FWO and KAS), of the dependence of the activation energy (*E*) on the mass loss (Δm) puts in evidence the different thermal behaviour of the investigated samples. Sample A exhibits *E* values independent on the heating rate only for the second decomposition step (corresponding to the decomposition of zinc acetate), while sample B exhibits *E* values dependent on the heating rate for all three decomposition steps. For sample A, *E* values do not change with Δm, while for sample B, *E* values depend on Δm in all decomposition steps. It turns out that only the second decomposition step of sample A is characterized by a single kinetic triplet (E, $Af(\alpha)$).

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