

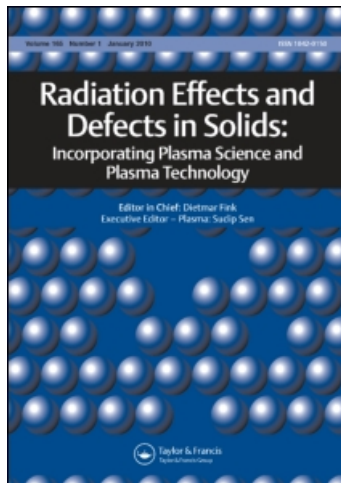
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Radiation Effects and Defects in Solids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713648881>

Kinetic analysis of the thermal decomposition of pristine and γ -irradiated zinc uranyl acetate

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To cite this Article Al-muhaimid, T. I. A. , Al-qunaibit, M. H. , Al-farhan, K. A. and Mahfouz, R. M. (2004) 'Kinetic analysis of the thermal decomposition of pristine and γ -irradiated zinc uranyl acetate', *Radiation Effects and Defects in Solids*, 159: 11, 613 – 635

To link to this Article: DOI: 10.1080/10420150412331330511

URL: <http://dx.doi.org/10.1080/10420150412331330511>

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KINETIC ANALYSIS OF THE THERMAL DECOMPOSITION OF PRISTINE AND γ -IRRADIATED ZINC URANYL ACETATE

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(Received 27 October 2004; In final form 1 November 2004)

Thermal decomposition of pristine and γ -irradiated zinc uranyl acetate was investigated in air using isothermal and dynamic thermogravimetric techniques. The decomposition proceeded via one major process with the formation of triuranates ZnU_3O_{10} as solid residues. Kinetic analysis of isothermal data, when compared with various solid-state reaction models, showed that the decomposition reaction is best fitted by the phase-boundary model. Kinetic analysis of the dynamic TG curves was discussed with reference to integral methods of modified Coats and Redfern equations. Kinetic and thermodynamic parameters were calculated and evaluated. IR spectroscopy and X-ray powder diffraction techniques were employed to follow the chemical composition of solid residue at different calcination temperatures. The results display that the triuranate ZnU_3O_{10} starts forming by calcination of zinc uranyl acetate at temperatures $>300^\circ\text{C}$ and undergoes decomposition at higher temperatures ($>600^\circ\text{C}$) with the formation of U_3O_8 . The results were evaluated regarding the utilization of zinc uranyl acetate as an important source of diuranates and triuranates.

Keywords: Thermogravimetry; Isothermal; Non-isothermal; Infrared spectroscopy; X-ray diffraction

1 INTRODUCTION

Thermal decomposition of solids is an important field of solid-state chemistry with wide technical applications such as fabrication of surface-active metal oxides to use in the catalysis and in the preparation of well-defined double or multi-component oxides, which show interesting optical and electrical properties [1].

Metal–uranyl acetate systems represent an important source for preparing metal–uranium–oxygen systems such as uranate, diuranates and triuranates. The oxy–uranium compounds have wide applications in both technological and military fields. The study of the thermal behavior of metal–uranyl–oxy compounds is therefore of significant importance with regards to economic utilization of these systems [2–5].

Only a few studies have appeared in the literature on the thermal properties of metal–uranyl–oxy systems, with little attention on the kinetics of thermal decomposition [6–8]. In the present study, we report the kinetic results of thermal decomposition of un-irradiated (pristine) and pre- γ -irradiated zinc uranyl acetate using both isothermal and dynamic thermogravimetric

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techniques. The chemical composition of the solid residue of the decomposition was analyzed using infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) techniques.

2 EXPERIMENTAL

Zinc uranyl acetate samples used in the present investigation were of BDH reagent grade and used without any further chemical or physical treatment. The samples were dried at 80°C for 1 day to ensure complete dehydration. The thermal decomposition was followed by non-isothermal (dynamic) and isothermal thermogravimetric techniques using a TGA-7 (Perkin-Elmer) thermogravimetric analyzer. For irradiation, the samples were encapsulated under vacuum in glass vials and were exposed to successively increasing doses of γ -irradiation at constant intensity using a Co-60 γ -ray cell 220 (Nordion INT-INC) at a rate of 10^4 Gy/h. The source was calibrated with a Fricke ferrous sulfate dosimeter, and the dose rate in the irradiated samples was calculated by applying appropriate corrections on the basis of photon mass attenuation and energy-absorption coefficient for the sample and the dosimeter solution [9]. IR spectra were recorded as KBr pellets using a Perkin-Elmer 1000FT-IR spectrophotometer. XRD measurements were carried out on a Siemens D5000 X-ray diffractometer using a nickel filter ($\text{CuK}\alpha$ $\lambda = 1.5418$ Å).

3 RESULTS AND DISCUSSION

Figure 1 shows typical TG-DTG and DTA curves of the pristine material. The TG curves show that the decomposition of the compound occurs in one major step in the temperature range

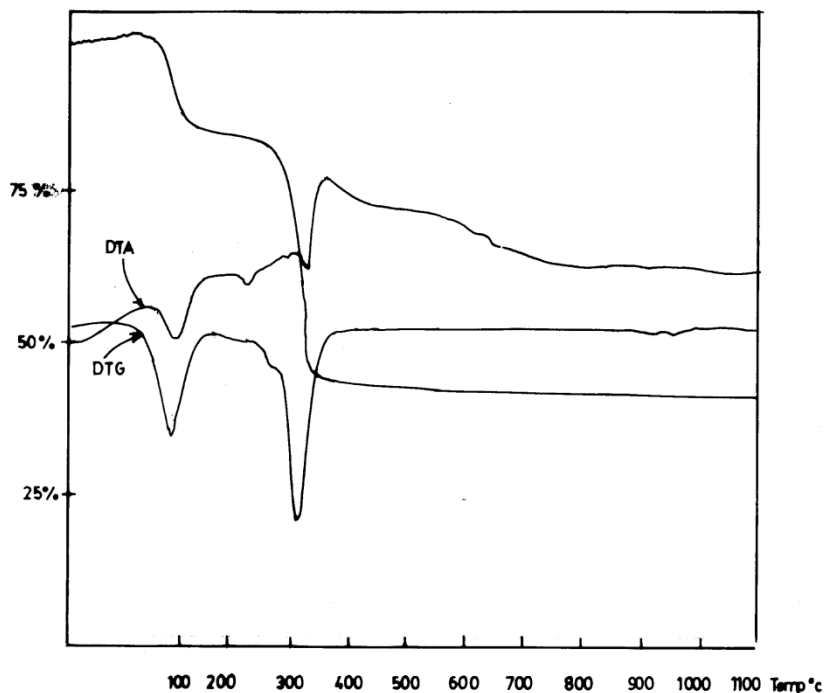


FIGURE 1 Typical TG-DTG and DTA curves of un-irradiated zinc uranyl acetate.

(200–350 °C) corresponding to the formation of volatile products and a solid of mixture oxides. Two endothermic peaks, as shown in the DTA curve, accompanied the decomposition. This behavior reveals that the main decomposition process involves two steps. The thermogram displays a minor gain in weight in the range of 300–600 °C accompanied by a small exothermic peak due to the possible formation of $\text{ZnU}_3\text{O}_{10}$. The triuranate undergoes decomposition in the range 800–1100 °C in one major step with the formation of U_3O_8 and ZnO as final products. No change in the decomposition behavior of the γ -irradiated samples was noticed, and the decomposition proceeded in the same manner as in the case of un-irradiated (pristine) samples.

3.1 Isothermal Decomposition

Isothermal decomposition of pristine and pre- γ -irradiated zinc uranyl acetate samples was studied in the temperature range (220–250 °C). Figures 2 and 3 show α vs. t curves of the decomposition at the temperatures, where α is the fraction decomposed at decomposition time, t . The curves show an increase in the fraction decomposed α with an increase in the decomposition time up to a maximum value depending on the temperature investigated. Shortening of the induction period and acceleration in time required to reach α_{max} at a given temperature was observed markedly in the decomposition behavior of pre-irradiated samples. That behavior could be attributed to the formation of additional nucleation sites. The nucleation centers enhance all of the decomposition stages (induction period, acceleratory region and decay stage). The isothermal α/t data for the main process, *i.e.*, the acceleratory region of zinc uranyl acetate decomposition ($0.05 < \alpha < 0.99$) was analyzed according to the various kinetic mechanisms cited in Table I [10].

Under isothermal conditions, the rate constant k is independent of the reaction time and so $kt = g(\alpha)$. A plot of $g(\alpha)$ vs. t should give a straight line if the correct form of $g(\alpha)$ vs. t is reached. The function $g(\alpha)$ depends on the mechanism controlling the reaction, the size and shape of the reacting particles. In a diffusion-controlled reaction: D_1 is a function for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D_2 is a function for a two-dimensional diffusion-controlled process into a cylinder; D_3 is Jander's equation for diffusion-controlled reaction in a sphere and D_4 is a function for a diffusion-controlled reaction starting on the exterior of a spherical particle. In phase-boundary-controlled reactions, the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously. Then, the equation relating α and t is the R_2 function for a circular disc reacting from the edge inward and the function R_3 for a sphere reacting from the surface inward. If the solid-state reaction follows first-order kinetics (F_1 function), then the rate-determining step is the nucleation process and there is an equal probability of nucleation at each active site. In phase-boundary reactions, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of the product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As the nuclei grow larger, they must eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and Erofe'v, who have given the functions A_2 and A_3 , respectively.

Our results as shown in Figures 4 and 5 indicate that isothermal data of both pristine and pre-irradiated zinc uranyl acetate obey the phase-boundary mechanism (R_2) kinetic model.

3.2 Non-isothermal Decomposition

The thermal behavior of zinc uranyl acetate was also investigated under constant heating rate conditions. Figures 6 and 7 show the results obtained from dynamic measurements for samples studied in nitrogen at different heating rates of 5, 10, 15 and 20 °C/min. In the analysis of

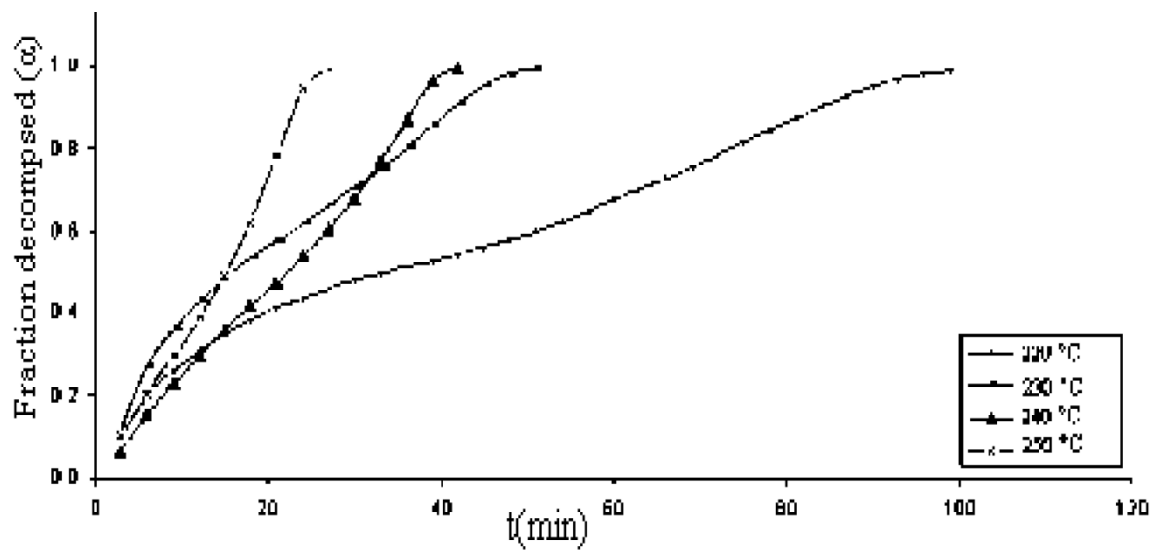


FIGURE 2 α/t curves of isothermal decomposition of un-irradiated zinc uranyl acetate.

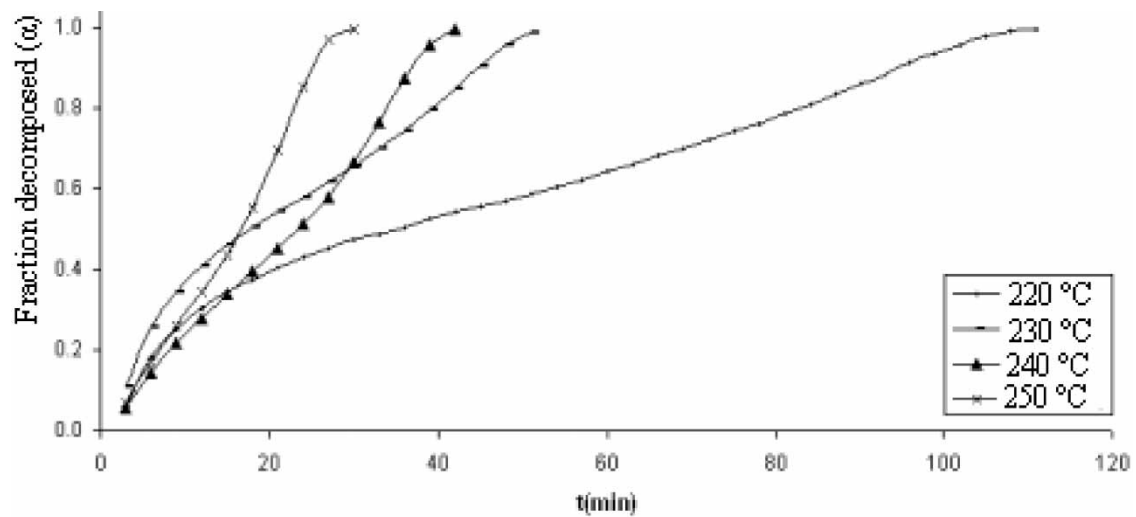


FIGURE 3 α/t curves of isothermal decomposition of pre-irradiated zinc uranyl acetate (total dose 6×10^6 Gy).

TABLE I Mechanistic equations examined in this work.

Equation	Function	Function
One-dimensional diffusion	α^2	D ₁
Two-dimensional diffusion	$(1 - \alpha) \ln(1 - \alpha) + \alpha$	D ₂
Jander equation, three-dimensional diffusion	$[1 - (1 - \alpha)^{1/3}]^2$	D ₃
Guistling–Brounshtein equation, three-dimensional diffusion	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	D ₄
Two-dimensional phase-boundary reaction	$1 - (1 - \alpha)^{1/2}$	R ₂
Three-dimensional phase-boundary reaction	$1 - \ln(1 - \alpha)^{1/3}$	R ₃
First-order kinetic	$\ln(1 - \alpha)$	F ₁
Prout–Thompkins branching nuclei	$\ln[\alpha/(1 - \alpha)]$	A ₁
Random nucleation: Avrami equation	$-\ln(1 - \alpha)^{1/2}$	A ₂
Random nucleation: Erofe'v equation	$-\ln(1 - \alpha)^{1/3}$	A ₃

dynamic TG curves, the temperature rate is set to a constant value β and the function $g(\alpha)$ is given by Doyle's equation [11, 12]

$$g(\alpha) = \left(\frac{A}{B}\right) \int_0^t \exp -\frac{E}{RT} dT \frac{AE}{R\beta} P(x). \quad (1)$$

The function $P(x)$ has been defined as

$$P(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u} du}{u}, \quad (2)$$

where $u = E/RT$ and x is the corresponding value of u of which a fraction α of material has decomposed. In the modified Coats–Redfern [12] method, the function $g(\alpha)$ is approximated by the form

$$\log\left(\frac{g(\alpha)}{T^2}\right) = \log\left(\frac{AR}{EB}\right) - \left(\frac{E}{2.3RT}\right). \quad (3)$$

Accordingly, $\log[g(\alpha)/T^2]$ is to be calculated for all possible mechanisms cited in Table I and plotted against $1/T$. The best straight line obtained using LR analysis determines the operating mechanism. The dynamic data using the modified Coats and Redfern model are best fitted to the R₂ and D₂ models, and the results are shown in Figures 8 and 9.

3.3 Kinetic and Thermodynamic Parameters

The general disadvantage of the dynamic thermal analysis is the fact that in many cases more than one function $g(\alpha)$ fits the experimental results. The selection of the proper model is then practically impossible, leading to the inability to estimate the real kinetic parameters. Recently, the view that the combined use of isothermal and non-isothermal method for thermal data kinetic analysis as the proper solution has been more frequently expressed. Table II lists E_a and $\ln A$ values calculated from both isothermal and dynamic experiments, using for $g(\alpha)$ the R₂ phase-boundary model for both pristine and pre-irradiated materials.

It is noteworthy that the kinetic parameters such as the activation energy, the pre-exponential factor and the reaction order do not hold in most solid-state heterogeneous reactions as these parameters are initially derived from equations for homogeneous reactions in the gas or liquid phase. The thermal decomposition of a solid may be a complicated process which involves many steps such as a change of the crystal lattice or its destruction, disintegration and formation of compounds, desorption and diffusion of gaseous products, dehydration, fusion and sublimation. As experimental factors have a great effect on the solid-state reactions, the application of the equations mentioned in Table I to the kinetics of solid-state reactions is of

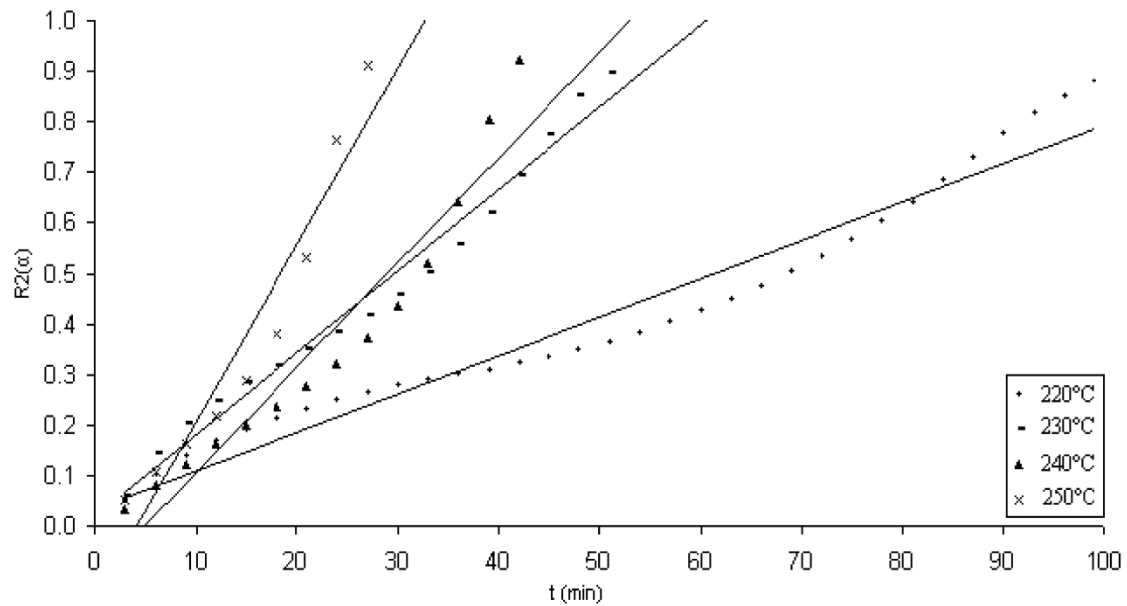


FIGURE 4 Kinetic analysis of α/t curves of isothermal decomposition of un-irradiated zinc uranyl acetate according to the straight-line method (R_2 model).

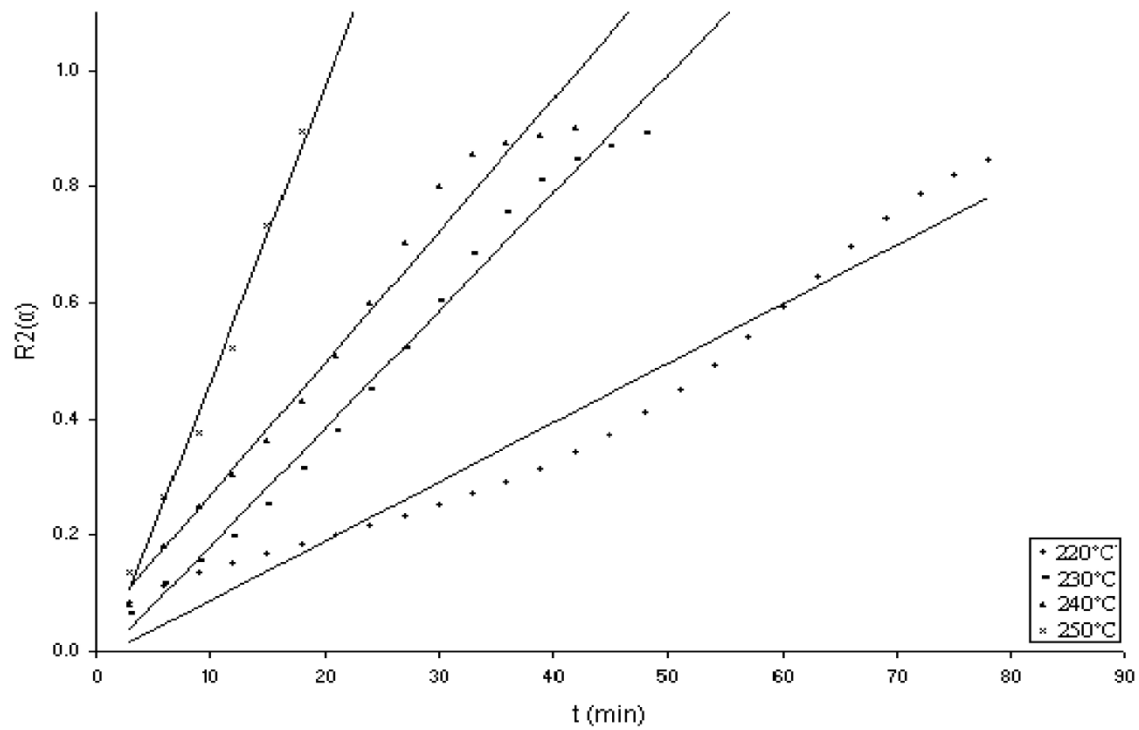


FIGURE 5 Kinetic analysis of α/t curves of isothermal decomposition of pre-irradiated zinc uranyl acetate (total dose 6×10^6 Gy) according to the straight-line method (R_2 model).

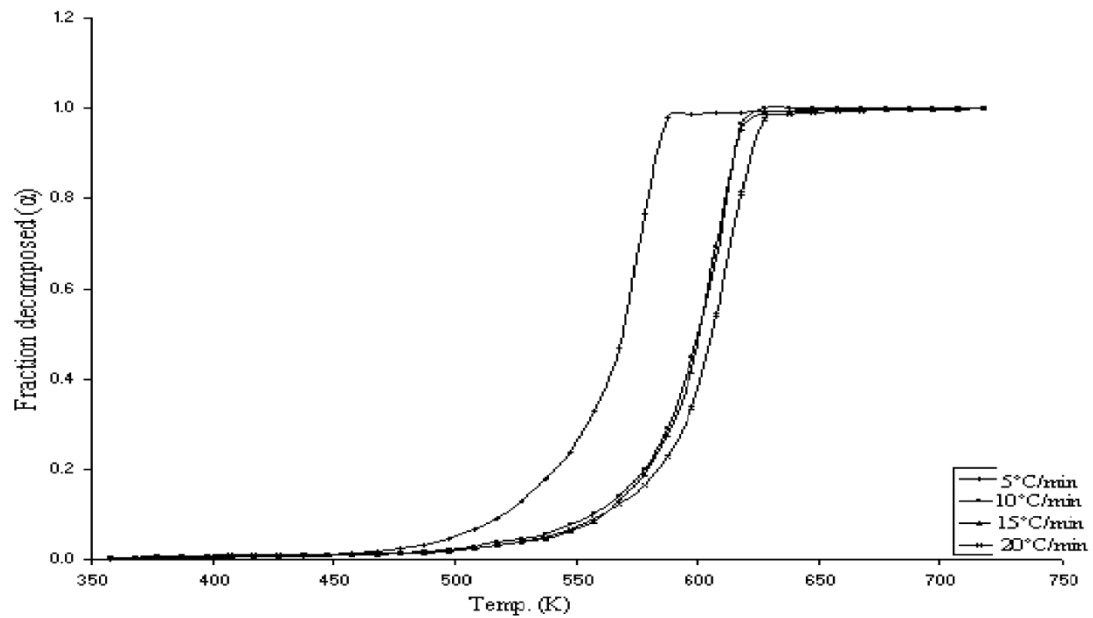


FIGURE 6 α/T curves of non-isothermal decomposition of un-irradiated zinc uranyl acetate.

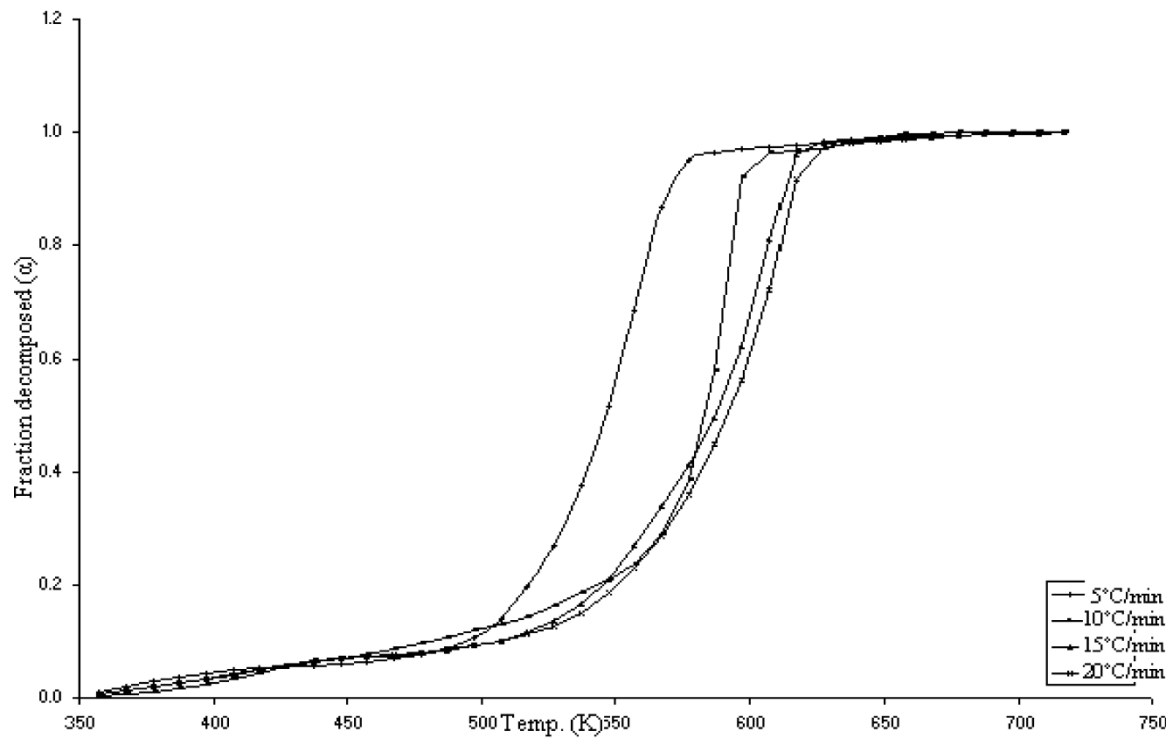


FIGURE 7 α/T curves of non-isothermal decomposition of pre-irradiated zinc uranyl acetate (total dose 10^4 Gy).

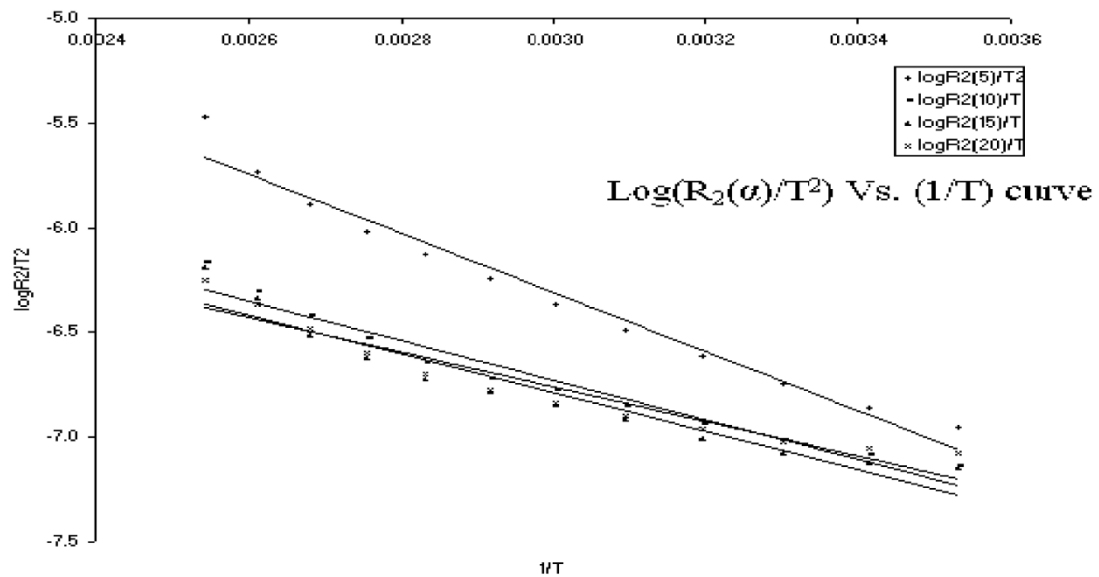


FIGURE 8 Kinetic analysis of α/T curves of non-isothermal decomposition of un-irradiated zinc uranyl acetate according to modified Coats-Redfern equation (R_2 model).

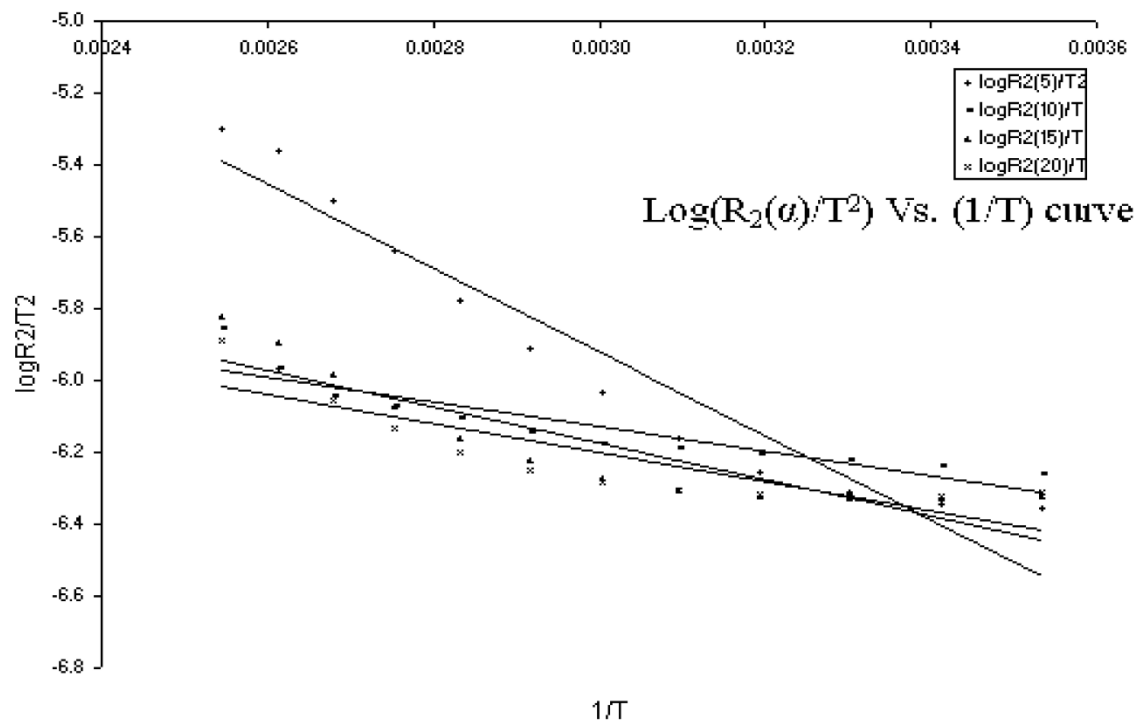


FIGURE 9 Kinetic analysis of α/T curves of non-isothermal decomposition of pre-irradiated zinc uranyl acetate (total dose 6×10^6 Gy) according to modified Coats–Redfern equation (R_2 model).

TABLE II Kinetic and thermodynamic parameter of the decomposition of zinc uranyl acetate.

	<i>Kinetic parameters</i>		<i>Thermodynamic parameters</i>
	<i>Isothermal</i>	<i>Non-isothermal</i> ($\beta = 10^\circ\text{C min}^{-1}$)*	
Kinetic model	R ₂ model	R ₂ and D ₂ model	
E_a (kJ mol ⁻¹)	103.76 (105.66) [†]	18.10 (662) [†]	
ln A (min ⁻¹)	20.52 (21.22) [†]	4.38 (0.61) [†]	
$\Delta S^{\neq 0}$ (kJ mol ⁻¹)			-1.25 (-1.24) [†]
$\Delta H^{\neq 0}$ (J mol ⁻¹)			99.54 (101.44) [†]

*Only one heating rate data (10°C min⁻¹) are reported for comparison.

[†]The values between brackets are for pre-irradiated sample with 6×10^6 Gy total γ -ray dose.

limited value, the kinetic parameters are not well defined, and their meaning is not always clear. The kinetic parameters are, therefore, only empirical constants giving the best fit to the experimental data and do not have any deeper physical meaning. As a consequence, the validity of the kinetic data is limited to the conditions under which the process is studied. Nevertheless, as individual TG curves can frequently be well-characterized by means of kinetic parameters, the derivation of these parameters is important and should be considered as a first step in the description of the kinetics of these reactions. It is now recognized that real solid-state reactions are often too complexes to be described in terms of a single pair of Arrhenius parameters and the traditional set of reaction models. This has inspired development of new computational techniques that make allowance of multi-step kinetics [13–15].

The use of single heating rate data for the determination of kinetic parameters should be avoided; model-fitting methods that use multi-heating rate data and assume a multi-step nature of the process can describe the course of a solid reaction sufficiently well. Owing to the fact that non-isothermal parameters are calculated from the data obtained in a much wider temperature range, it is logical to use these for the prediction of isothermal runs. The opposite procedure may be erroneous. The significance differences in the values of E_a calculated by both isothermal and non-isothermal measurements in the present study clearly emphasize that the application of a single heating rate technique and model-fitting mechanism is of limited help to deduce the correct and adequate kinetic parameters. The multi-step process using the multi-heating rate technique and model-free methods are rather typical for reactions of solids [16].

Entropy and enthalpy values of the main decomposition process were calculated using the following equation

$$\ln \frac{K}{T} = \frac{-\Delta H^{\neq 0}}{RT} + \ln \frac{R}{Nh} + \frac{\Delta S^{\neq 0}}{R}, \quad (4)$$

where K the rate constant, R is the gas constant, T the absolute temperature, N the Avogadro's number and h the Plank's constant. Plotting $\ln K/T$ against $1/T$, the slope and intercept give $\Delta H^{\neq 0}$ and $\Delta S^{\neq 0}$, respectively.

The calculated values are also included in Table II. The close values of the thermodynamic parameters obtained for both un-irradiated and pre-irradiated zinc uranyl acetate emphasize that the phase transitions occurring during the thermal decomposition of zinc uranyl acetate

are similar for both of the two samples investigated. Further studies concerning application of the computational methods that employ multi-heating rate data and allow for treating multi-step processes on the present isothermal and non-isothermal are in progress. The result will appear as a second publication of this study.

3.4 IR and XRD Measurements

The physical and chemical changes induced by γ -irradiation in zinc uranyl acetate were followed by recording IR spectra of the material before and after γ -irradiation as well as XRD measurements. The important IR bands and their assignments are listed in Table III and their spectra are shown in Figures 10 and 11. A decrease in the intensity of most vibration bands was observed in the spectrum of pre- γ -irradiated samples with total γ -ray dose of 10^6 Gy. The bands assigned to ν_{COO^-} , $\nu_{\text{U}-\text{O}}$ and $\nu_{\text{Zn}-\text{O}}$ were more affected by irradiation than the other bands in the spectrum. The decrease in intensity of these bands could be attributed to the bond scission and degradation caused by γ -irradiation [17–19].

XRD pattern of zinc uranyl acetate before and after irradiation are shown in Figures 12 and 13. Crystallinity of the compound was affected by irradiation. The X-ray data are included in Table IV.

XRD and IR techniques were also employed to identify the chemical composition of the solid residue from different stages of the thermal decomposition of zinc uranyl acetate. In this respect, the samples were calcinated at three different calcination temperatures 300, 600 and 900 °C. The solid products of the calcinations were subjected to investigation using the earlier mentioned techniques.

IR absorption spectra of the residues from different calcinations temperatures for both un-irradiated and γ -irradiated material are shown in Figures 14–16. The spectra display characteristic bands assigned to $\nu_{\text{Zn}-\text{O}}$ and $\nu_{\text{U}=\text{O}}$ at 440 and 895 cm^{-1} , respectively, for

TABLE III Characteristic IR frequencies of un-irradiated zinc uranyl acetate.

Assignment	Band position (cm^{-1})
$\nu_{\text{as}}(\text{COO}^-)$	1,553
$\nu_{\text{s}}(\text{COO}^-)$	1,456
$\nu_{\text{as}}(\text{UO}_2^+)$	931
$\nu(\text{UO}^-)$	$Sh \sim 503$
$\nu(\text{ZnO}^-)$	522

TABLE IV D-values and their relative intensities of recorded un-irradiated zinc uranyl acetate.

$d(\text{\AA})$	Intensity (I/I_0)
7.49	100
7.78	53
4.50	49
3.92	31
3.58	30
3.46	21
2.93	19
4.02	17

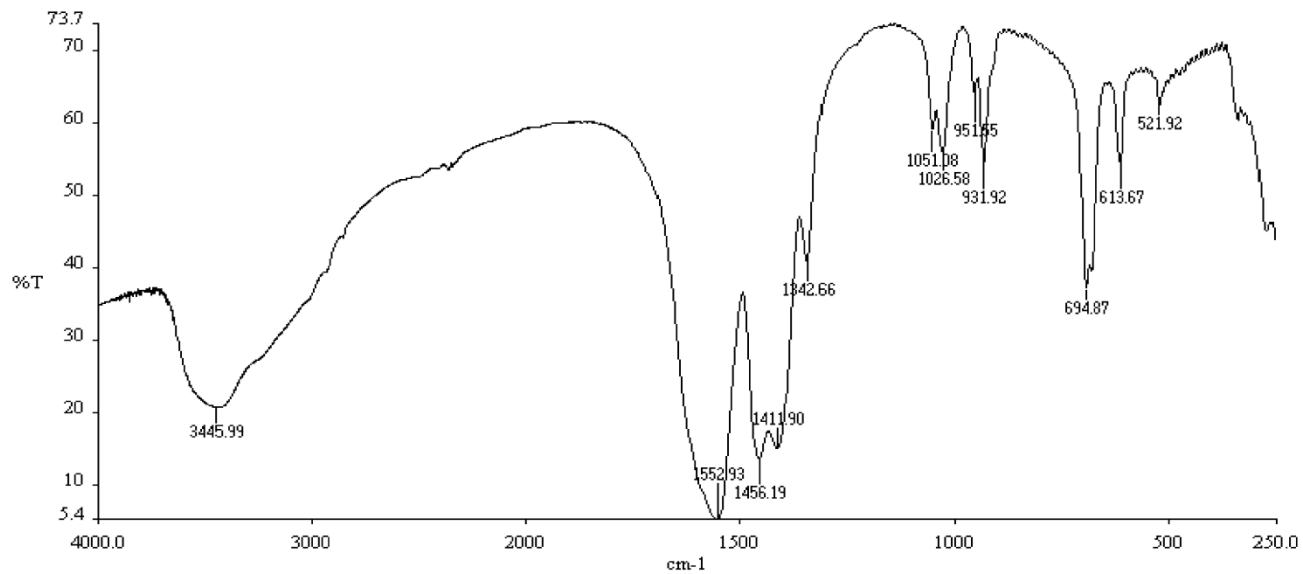


FIGURE 10 The IR spectrum of un-irradiated zinc uranyl acetate.

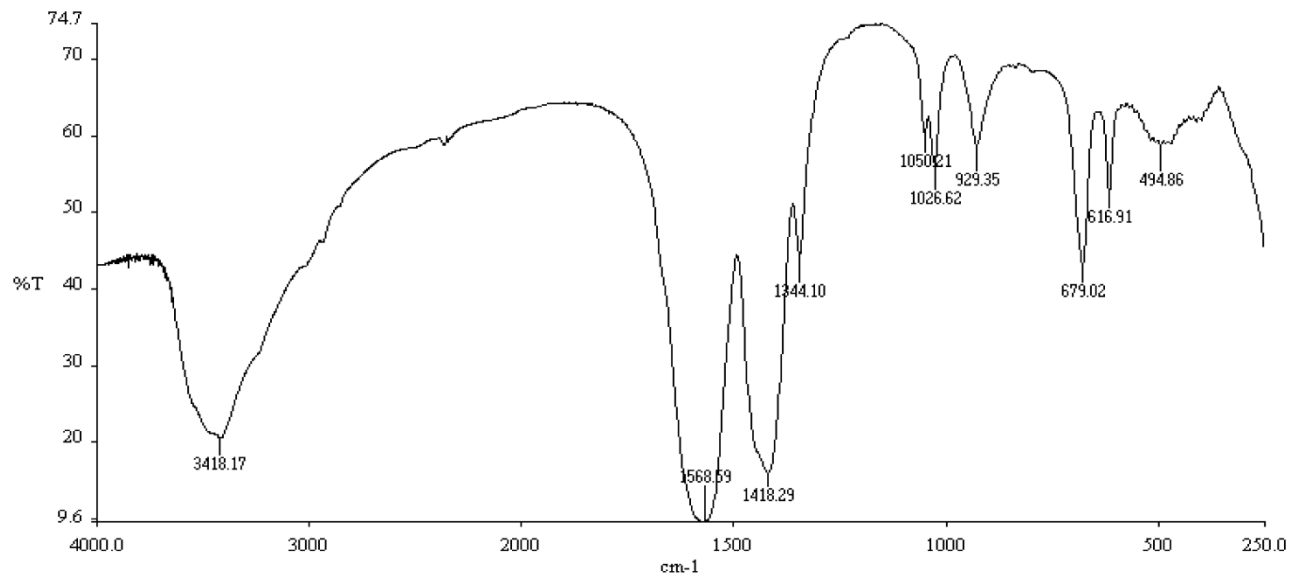


FIGURE 11 The IR spectrum of pre-irradiated zinc uranyl acetate (total dose 6×10^6 Gy).

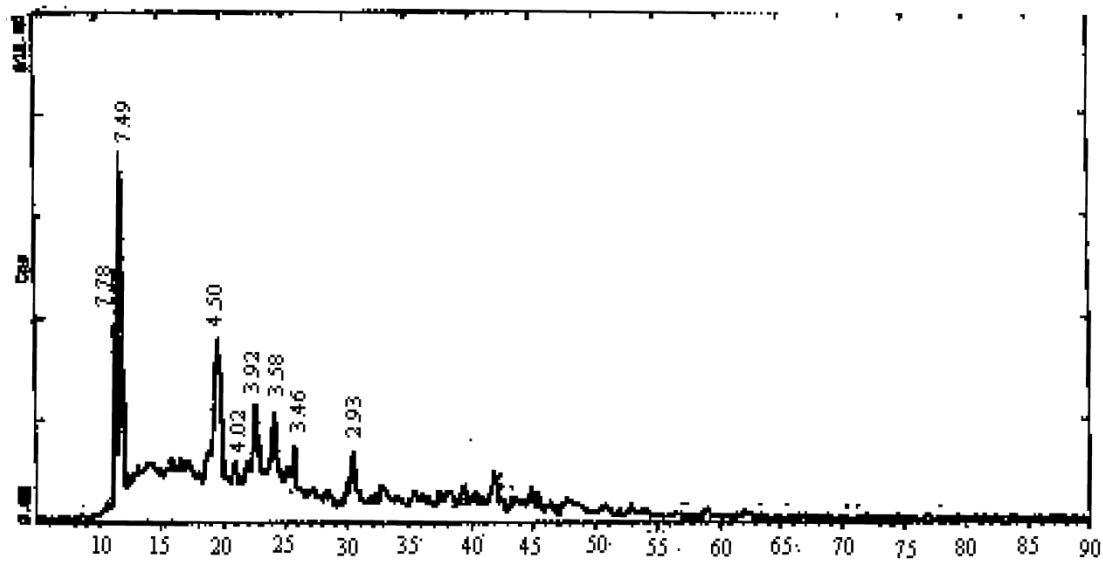


FIGURE 12 XRD pattern of un-irradiated zinc uranyl acetate.

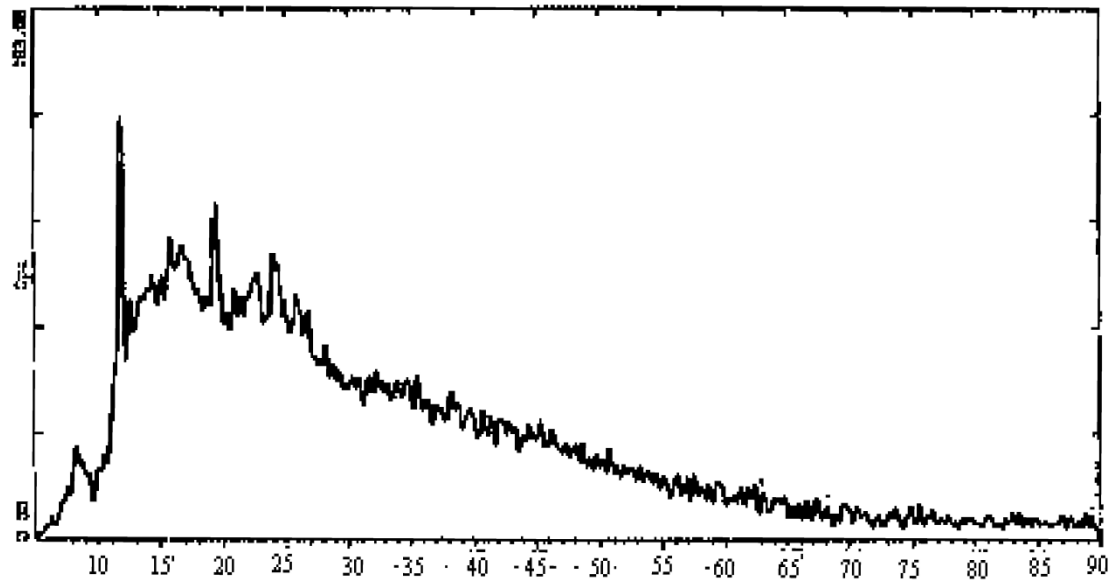


FIGURE 13 XRD pattern of pre-irradiated zinc uranyl acetate (total dose 6×10^6 Gy).

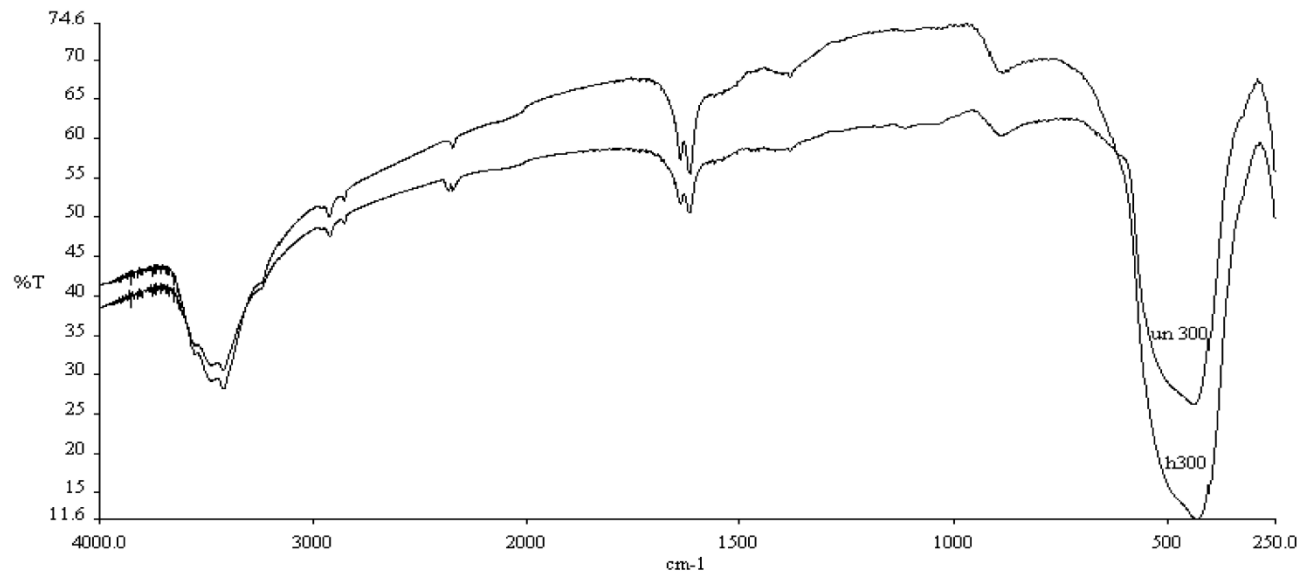


FIGURE 14 The IR spectra of pre-irradiated (6×10^6 Gy total dose) (bottom spectrum), as compared to the un-irradiated (top spectrum) zinc uranyl acetate calcinated at 300 °C.

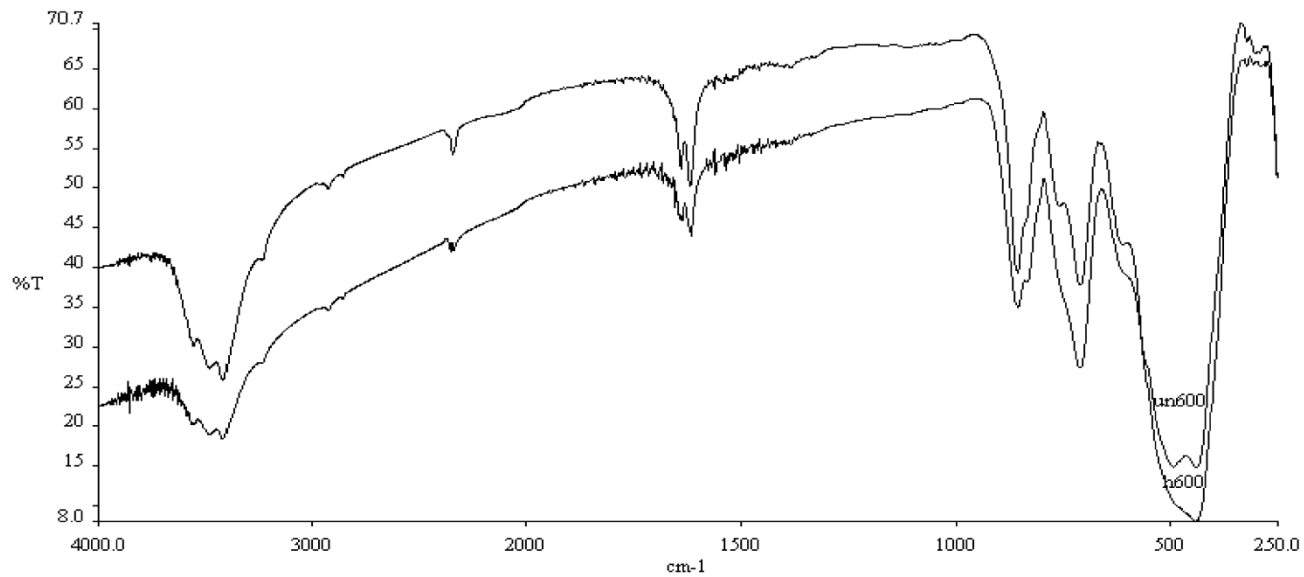


FIGURE 15 The IR spectra of per-irradiated (6×10^6 total dose) (bottom spectrum) compared to the un-irradiated (top spectrum) of zinc uranyl acetate calcinated at 600 °C.

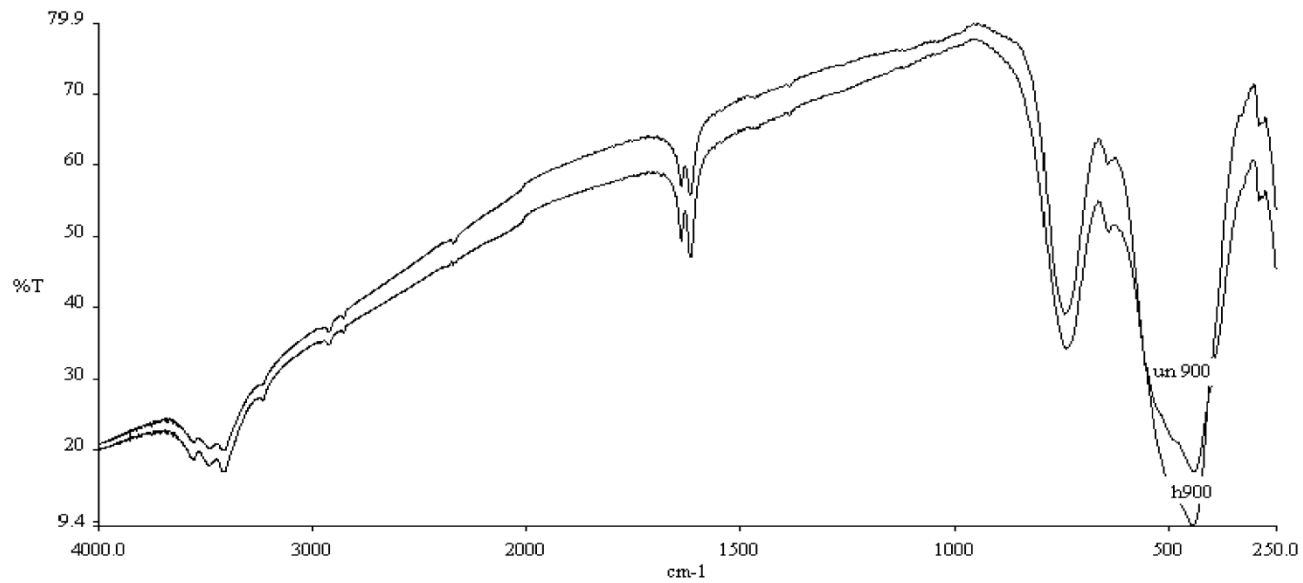


FIGURE 16 The IR spectra of per-irradiated (6×10^6 total dose) (bottom spectrum) compared to un-irradiated (top spectrum) of zinc uranyl acetate calcinated at 900 °C.

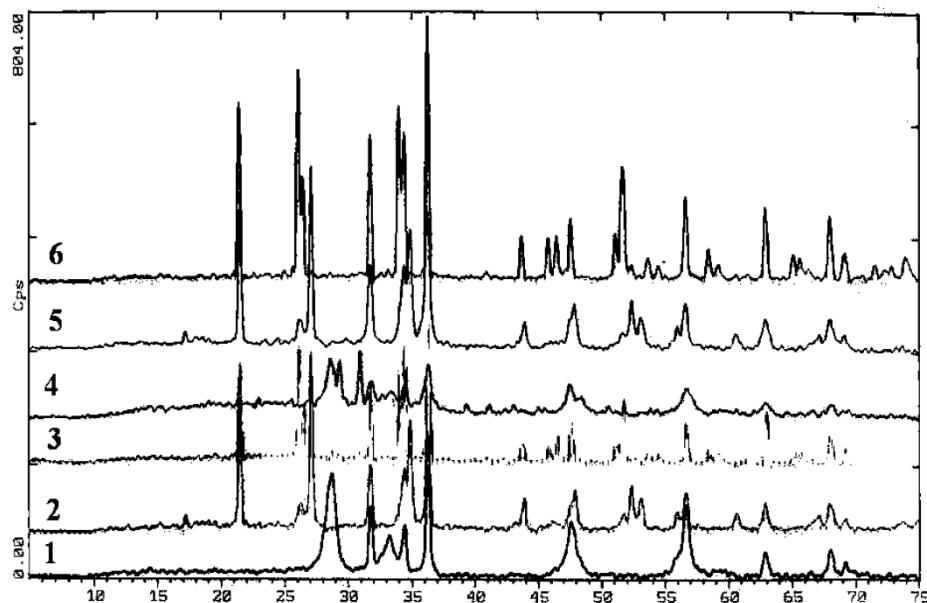


FIGURE 17 XRD patterns of un-irradiated zinc uranyl acetate calcinated at 300, 600 and 900 °C (1–3) compared to pre-irradiated samples (total dose 6×10^6 Gy) (4–6).

samples calcinated at 300 °C. At 600 °C, the IR spectra exhibit characteristic bands assigned to $\text{ZnU}_3\text{O}_{10}$ [2, 3]. At 900 °C, the spectra display bands of U_3O_8 in the range of 740 (s)–640 cm^{-1} (sh) and $\nu_{\text{Zn}-\text{O}}$ at 300 cm^{-1} . These results are in good coincidence with data reported in the literature.

The XRD patterns for the residue at 300, 600 and 900 °C of both pristine and pre- γ -irradiated zinc uranyl acetate are shown in Figure 17. They display almost the same feature at a given calcinations temperature for both un-irradiated and γ -irradiated samples of zinc uranyl acetates. Three different chemical compositions of the residue were detected at three investigated calcinations temperatures. At 300 °C, the patterns show a crystalline nature indicating that the products are ZnO/UO_2 reduced form mixtures. Continued heating of this residue resulted in the formation of a new crystalline phase, the triuranates $\text{ZnU}_3\text{O}_{10}$ as an oxidized form evidenced by the XRD patterns of the residue obtained at 600 °C. Decomposition of the new solid phase was preceded at higher temperatures with the formation of U_3O_8 as the final uranium solid product.

4 CONCLUSION

It is evident from the present study that zinc uranyl acetate decomposed in one major decomposition step with the formation of $\text{ZnO}/\text{U}_3\text{O}_8$ as final solid residues obtained at higher temperature. Triuranate $\text{ZnU}_3\text{O}_{10}$ could be obtained by calcinations of zinc uranyl acetate at temperature above 300 °C. The triuranates undergo decomposition at temperatures above 600 °C with the formation of U_3O_8 and ZnO . γ -Irradiation of zinc uranyl acetate up to 6×10^6 Gy total γ -ray dose has no effect on neither the behavior of decomposition nor the solid residues of the decomposition.

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