Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 404 (2003) 125–132
thermochimica acta
www.elsevier.com/locate/tca

Mass spectral studies on the mechanism of thermal decomposition of $Zn(NO_3)_2 \cdot nH_2O$

Barbara Małecka [a,*], Ryszard Gajerski [a], Andrzej Małecki [a], Małgorzata Wierzbicka [a], Piotr Olszewski [b]

[a] *Faculty of Materials Science and Ceramics, University of Mining and Metallurgy, 30 Mickiewicz Avenue, 30-059 Krakow, Poland*
[b] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 8 Niezapominajek Street, 30-239 Krakow, Poland*

Received 13 November 2002; received in revised form 30 January 2003; accepted 7 February 2003

Abstract

Thermal decomposition of $Zn(NO_3)_2 \cdot nH_2O$ ($n = 4$ and 6) was studied using TG, DTA and QMS techniques. Measurements were performed in helium and in dry air. It was found that the examined reaction is a multi-step process with overlapping stages. The whole process depends on the rate of heating. Degradation of nitrate(V) groups starts before all water of crystallisation is removed from the system. $Zn(NO_3)_2 \cdot 2Zn(OH)_2$ was identified as intermediate product of decomposition of $Zn(NO_3)_2 \cdot nH_2O$.

Keywords: Zinc nitrate; Thermal decomposition; QMS analysis

---

1. Introduction

The decomposition of $Zn(NO_3)_2 \cdot nH_2O$ is an important way to produce ZnO films from $Zn(NO_3)_2$ solutions by spray-pyrolysis technique. Thin-film zinc oxide continues to attract attention because of its low toxicity and many applications in solar cell technology and as thin-film gas sensors, varistors, phosphor for colour displays, transparent electrode in liquid crystal displays, components in photovoltaic devices and surface acoustic wave devices [1].

Four hydrated nitrates(V) of zinc exist: $Zn(NO_3)_2 \cdot H_2O$, $Zn(NO_3)_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ with melting temperatures of 343.9, 328.6, 317.9 and 309.3 K, respectively [2]. The hydrated salts form in the reaction between ZnO and HNO_3 in aqueous solution.

Anhydrous zinc nitrate(V) is not in equilibrium with water under any conditions. It is obtained by reaction of metallic Zn with N_2O_4. $Zn(NO_3)_2$ is a complex compound with NO_3^- ions as bidentate ligands. This explains why anhydrous $Zn(NO_3)_2$ is slightly volatile in vacuum and decomposes rapidly at 623 K [3].

$[Zn(H_2O)_6](NO_3)_2$ crystallises in the orthorhombic space group *Pnma* and is isotypic with $[Mn(H_2O)_6](NO_3)_2$ [4]. $[Zn(H_2O)_4](NO_3)_2$ is monoclinic (space group $P2_1/n$) [5] and is isotypic with $[Mn(H_2O)_4](NO_3)_2$ [6]. A direct bonding of the nitrate group to the zinc cation is not reported.

$Zn(NO_3)_2 \cdot 6H_2O$ undergoes partial dehydration at a partial pressure of water equal to 13 Pa at 305 K (water partial pressure above 80% sulphuric acid) first to zinc nitrate(V) tetrahydrate and then to dihydrate. At a water partial pressure 10^{-2} to 10^{-3} Pa in the temperature range 25–58 °C dehydration goes to

---

* Corresponding author. Tel.: +48-12-617-24-70; fax: +48-12-617-24-93.
E-mail address: bmalecka@uci.agh.edu.pl (B. Małecka).

doi:10.1016/S0040-6031(03)00101-1

the monohydrate without any intermediate hydrate [7].

During thermal decomposition of $Zn(NO_3)_2{\cdot}6H_2O$, the following solid products were reported [8]:

$$Zn(NO_3)_2 \cdot 6H_2O \rightarrow Zn(NO_3)_2 \cdot H_2O$$

$$Zn(NO_3)_2 \cdot H_2O \rightarrow Zn(NO_3)_2 \cdot 2Zn(OH)_2$$

$$Zn(NO_3)_2 \cdot 2Zn(OH)_2 \rightarrow ZnO$$

$Zn(NO_3)_2{\cdot}2Zn(OH)_2$ forms during slow evaporation of zinc nitrate(V) hexahydrate solution at 393 K in air [9]. $Zn(NO_3)_2{\cdot}Zn(OH)_2{\cdot}2H_2O$ is another intermediate phase synthesised by slow dehydration of $Zn(NO_3)_2{\cdot}6H_2O$ at 338 K in air [10]. Structural investigations of hydroxy-nitrates of zinc showed that their layered structure is a modification of the layered structure of adequate hydroxides in which NO_3^- groups substitute OH^- groups [11,12]. There is common agreement that the final product of hydrated zinc nitrate(V) decomposition is ZnO.

The above considerations show that the mechanism of decomposition of $Zn(NO_3)_2{\cdot}6H_2O$ is not understood in detail. In the present paper an attempt has been made to explain this mechanism in the scope of broad research program concerning regularities of decomposition of oxy-salts of d-electron metals.

2. Experimental

Solid polycrystalline $Zn(NO_3)_2{\cdot}6H_2O$ (POCh Gliwice, Poland) of analytical grade was used in experiments as well as a precursor of lower hydrates. Zinc nitrate(V) hexahydrate was dried in a desiccator with 80% sulphuric acid (partial pressure of water equal to 13 Pa). After 3 months of drying at room temperature, zinc nitrate(V) tetrahydrate was obtained with these conditions, which was confirmed by XRD analysis.

Thermal decomposition was performed on an apparatus that enabled simultaneous recording of TGA and DTA signals (SDT 2960, TA INSTRUMENTS). This apparatus was connected on-line with a quadrupole mass spectrometer (QMD 300 THERMOSTAR, BALZERS) so that parallel analysis of gaseous products of the reaction was carried out. The energy of the ion source was 70 eV and a Faraday detector was used.

Ion currents for M/q values equal to 14, 16, 18, 30, 32, 44 and 46 were monitored (where M is molecular mass of particle, and q the particle charge). Selected M/q values correspond to the following parent ions and fragmentation ions which can form during decomposition of nitrates: N^+, O^+, H_2O^+, NO^+, $O_2{}^+$, $NO_2{}^+$. In case of low heating rates intensity of mass signals was very small therefore lines are not smooth. All intensities of ion peaks are first corrected for the background. The corrected ion intensities at the mass numbers M/q: 18, 30, 32, 44 and 46 correspond to the parent ions of H_2O, O_2, NO, N_2O and NO_2 and do not give directly the true intensities of these oxides because of fragmentation. To calculate the true intensities of these oxides, the fragmentation pattern and fragment ion intensities are taken from the fragmentation library [13] supplied along with the equipment.

Samples of 10–12 mg were heated in the platinum vessel with different heating rates in the range 0.1–5 $K\,min^{-1}$ in helium with a flow rate of 6 $dm^3\,h^{-1}$ (oxygen content in helium was about 10^{-4} vol.% and water saturation point was given as 233 K). The gas sampling capillary was placed directly above the vessel. All the data were gathered by an on-line computer system with the commercial software (TA INSTRUMENTS, BALZERS).

Some thermogravimetric measurements were performed on a MOM derivatograph using Q method of heating (providing the constant rate of mass loss) in dry air flow (sample mass used was about 500 mg).

Substrates and solid products of decomposition were analysed by X-ray diffraction using Cu Kα radiation (Siemens D5005, Bruker-AXS, Germany, with a high-temperature camera).

3. Results and discussion

The experiments were performed on commercial $Zn(NO_3)_2{\cdot}6H_2O$ as received as well as on $Zn(NO_3)_2{\cdot}4H_2O$ obtained by drying over sulphuric acid.

Fig. 1 shows the TG curve of $Zn(NO_3)_2{\cdot}6H_2O$ in dry air (10 ppm H_2O at ambient temperature). The rate of decomposition was equal to 0.1 $mg\,min^{-1}$ or 0.1 $K\,min^{-1}$ during the whole measurement. In the presented figure two evident *plateaus* appear on the TG curve corresponding to two stable compounds. Final product of the decomposition is ZnO. Its amount

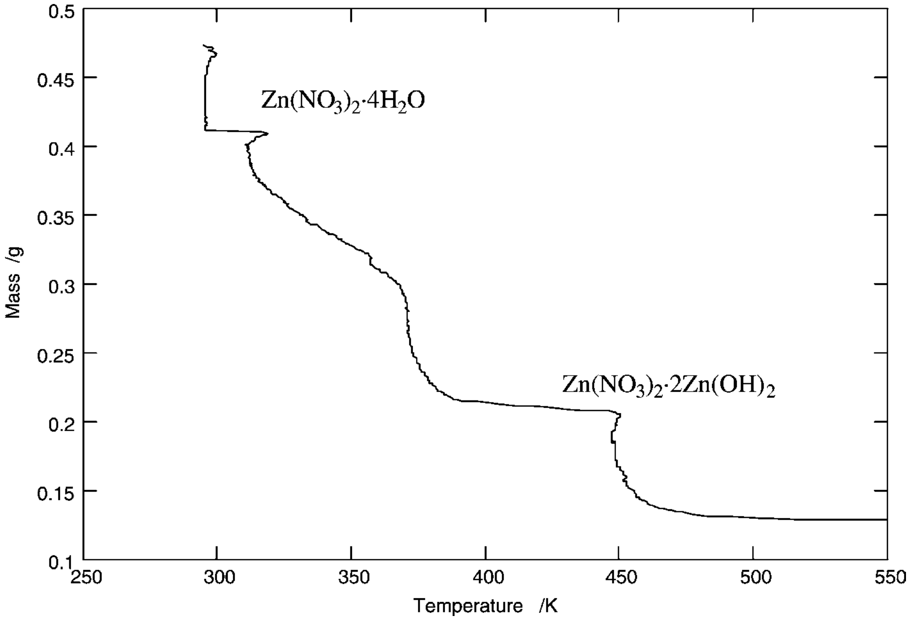

Fig. 1. TG curve of $Zn(NO_3)_2{\cdot}6H_2O$ decomposition in air at controlled rate of decomposition (0.1 mg min^{-1}, 0.1 K min^{-1}).

equals to 0.126 g was used to calculate the composition of the stable compounds revealed in this measurement. The first *plateau* in the temperature range 295–310 K is connected with the formation of zinc nitrate(V) tetrahydrate (mass from experiment: 0.408 g, calculated mass: 0.411 g). The second plateau is joined with the formation of $Zn(NO_3)_2{\cdot}2Zn(OH)_2$ stable in the temperature range 405–445 K (mass from experiment: 0.208 g, calculated mass: 0.204 g). This reaction is connected with simultaneous production of HNO_3:

$$3Zn(NO_3)_2 \cdot 4H_2O \rightarrow Zn(NO_3)_2 \cdot 2Zn(OH)_2 + 4HNO_3$$

During the thermal decomposition of hydrated zinc nitrate(V) under non-isothermal conditions with any rate of heating (even as low as 0.1 K min^{-1}), no distinct stages of decomposition can be observed on the TG curve. As examples, Figs. 2 and 3 show normalised TG and DTA curves and ion current intensities of H_2O^+, NO_2^+, NO^+ and O_2^+ obtained during $Zn(NO_3)_2{\cdot}4H_2O$ decomposition in helium at the rates of heating of 0.1 and 5 K min^{-1}, respectively. The signal for $M/q = 44$ ascribed to N_2O^+ ion was observed but its intensity was only 1% of NO_2^+ ion current intensity. This suggests that the amount of N_2O in gaseous products is very small and can be neglected in our considerations. Additionally, Fig. 4 shows similar character of the NO_2^+ mass spectrometric curve at different heating rates which indicates that the mechanism of decomposition does not depend on the heating rate.

$Zn(NO_3)_2{\cdot}4H_2O$ was placed in the crucible. After about half an hour of activities needed to stabilise response of QMS the sample lost some water of crystallisation. The amount of the water of crystallisation was calculated to be 3.6 molecules per molecule of zinc nitrate(V) at the beginning of heating. This suggests that dehydration of the sample in the flow of helium at room temperature leads to a mixture of hydrates. In the beginning of the decomposition, the sharp endothermic peak is seen on DTA curve at about 320 K connected with melting of sample which is consistent with the thermodynamic data. The next decomposition process proceeds in liquid state until majority of water is removed from the system. After removing almost all water the sample is a sticky substance easily absorbing water and melting in atmospheric air.

Some general statements can be formulated by analysing the spectra of the gaseous products of

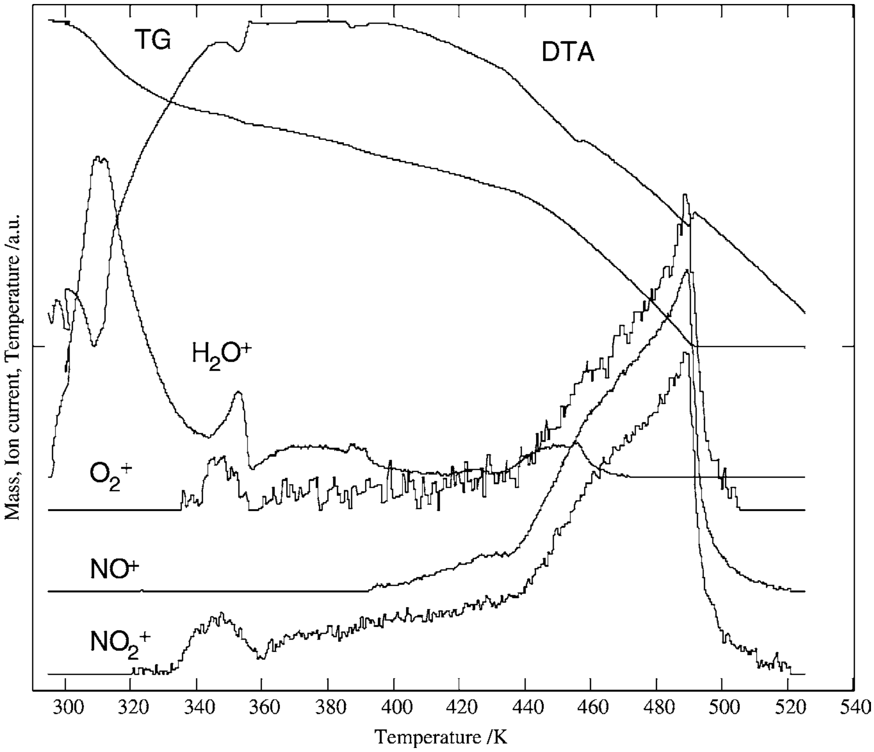

Fig. 2. Normalised TG and DTA curves and ion current intensities of gaseous products of $Zn(NO_3)_2{\cdot}4H_2O$ decomposition in helium (heating rate 0.25 K min^{-1}).

decomposition. Starting from ambient temperature the dehydration process begins which is manifested by mass loss and strong signal on the H_2O^+ intensity line.

The nitrate(V) group can decompose according to the following equation:

$$2NO_3^- \to x\mathrm{NO} + (2-x)NO_2 + \tfrac{1}{2}(x+1)O_2 + O^{2-}$$

The nitrogen oxides which arise during degradation of nitrate groups are noticed in the gaseous products starting at about 320 K (for heating rate 0.25 K min^{-1}). It must be emphasised that NO can be a primary product of NO_3^- decomposition as well as a product of fragmentation of NO_2 during ionisation in QMS, so the ionic current for $M/q = 30$ represents the total ion current from both sources. NO^+ spectra presented in Figs. 2–4 take into account the fragmentation effect with ratio $I_{\mathrm{NO(fragmented\,NO_2)}}/I_{\mathrm{NO_2}} = 2.727$ [13] (where I represents ionic current).

Ion current onset of NO^+, NO_2^+ and O_2^+ depends on heating rate and is observed for 5 K min^{-1} at about 370 K. This means that degradation of NO_3^- groups is observed before complete dehydration of the substance. Depending on the heating rate nitrogen oxides appear in gaseous products after removing about 50–80% H_2O. Quantitative estimation of the amount of gaseous products was performed by comparing the areas of adequate peaks. By the analysis of the ion current signal area of nitrogen oxides it can be concluded that only a small amount of NO_3^- groups (up to 20%) decompose before all water from the system is removed. Partial degradation of zinc nitrate(V) leads to formation of zinc hydroxide, zinc hydroxide nitrate or ZnO. The continuous weight loss seen on TG curve testifies that none of these compounds is present in pure form in the reacting product.

H_2O is evolved from the sample in two main stages. The first one ends at about 440–470 K, depending on the heating rate. It is manifested by the large peak on

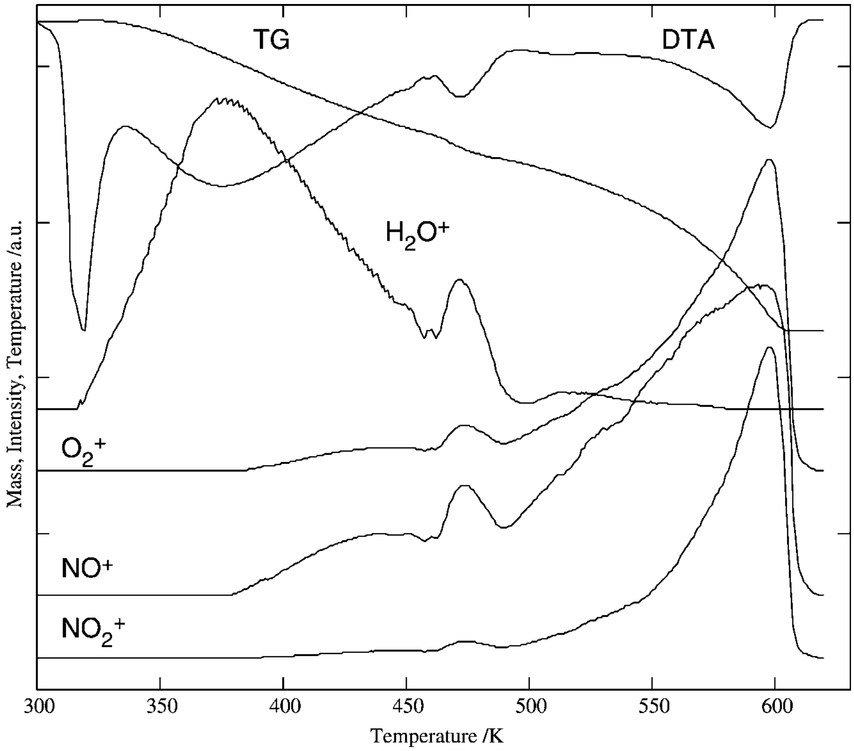

Fig. 3. Normalised TG and DTA curves and ion current intensities of gaseous products of $Zn(NO_3)_2 \cdot 4H_2O$ decomposition in helium (heating rate 5 K min^{-1}).

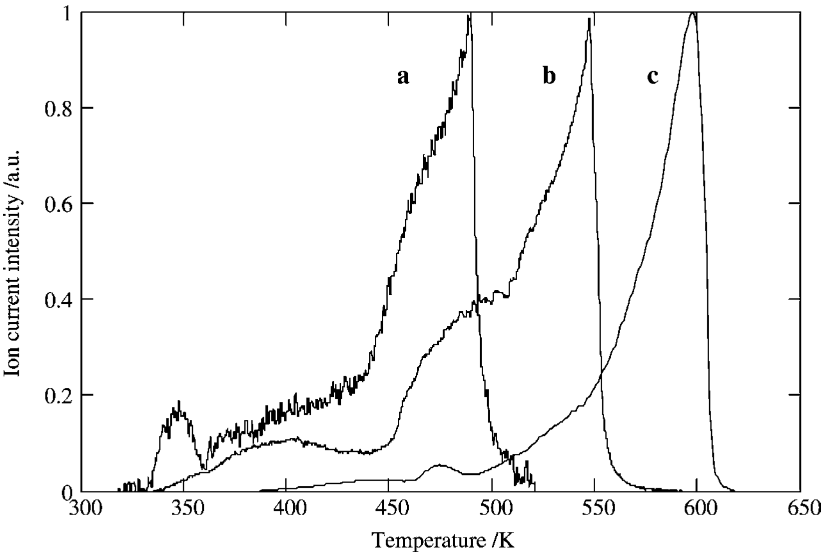

Fig. 4. Normalised ion current intensities of NO_2^+ of the decomposition of $Zn(NO_3)_2 \cdot 4H_2O$ at different heating rates: (a) 0.25 K min^{-1}; (b) 1 K min^{-1}; (c) 5 K min^{-1}.

H_2O^+ current line. Maximum of the second peak on H_2O^+ current line occurs at 450 K for heating rate of 0.25 K min^{-1} (at 480 K for heating rate of 5 K min^{-1}) and is connected with an endothermic effect on DTA line. The amount of water evolved in the second stage was estimated to about 10%. This second peak on the H_2O^+ current line can be a result of decomposition of hydroxyl ions because of the high temperature at this stage.

Decomposition of the main amount of nitrate(V) groups begins at the same temperature at which the second ion current signal of H_2O^+ is observed. It is at least two stage process. In the first stage, nitrogen oxides and oxygen are accompanied in gaseous products by water. In the second stage, only decomposition products of the nitrate group are detected. This can indicate that in the last stage of the decomposition products form which do not contain hydration water or hydroxyl ions. Basing on available data concerning compounds of zinc and nitrate ions the only substance of that composition is $Zn(NO_3)_2$.

$Zn(NO_3)_2\cdot 2Zn(OH)_2$ obtained as intermediate product during the decomposition of $Zn(NO_3)_2\cdot 6H_2O$ (Fig. 1) shows very similar stages as zinc nitrate(V) tetrahydrate in the last stages. Fig. 5 shows two stages of $Zn(NO_3)_2\cdot 2Zn(OH)_2$ decomposition. Only the first one is accompanied by H_2O^+ current signal due to decomposition. In the second stage, only nitrogen oxides and oxygen are present. The mass loss on the TG curve observed at about 370 K with a signal on H_2O^+ current intensity is connected with desorption of water.

These observations lead to conclusion that one of the intermediate products formed during non-isothermal decomposition of zinc nitrate(V) tetrahydrate is $Zn(NO_3)_2\cdot 2Zn(OH)_2$. This was confirmed by results of XRD analysis performed in the high-temperature camera (Fig. 6). Crystalline $Zn(NO_3)_2\cdot 2Zn(OH)_2$ appears at about 340 K and exists in the mixture up

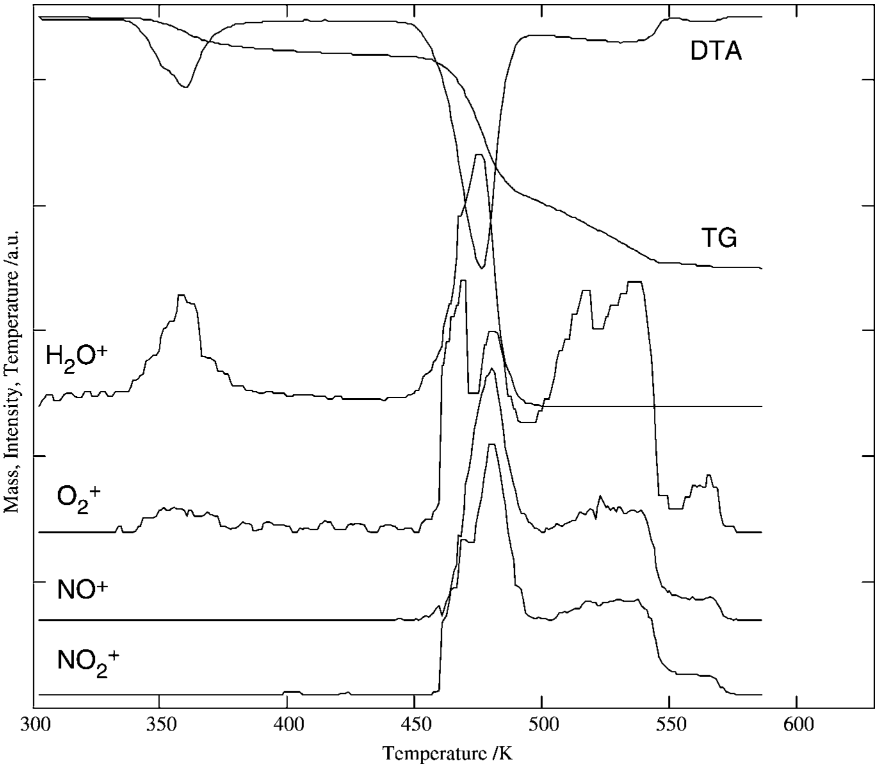

Fig. 5. Normalised TG and DTA curves and ion current intensities of gaseous products of $Zn(NO_3)_2\cdot 2Zn(OH)_2$ decomposition in helium (heating rate: 2 K min^{-1}).

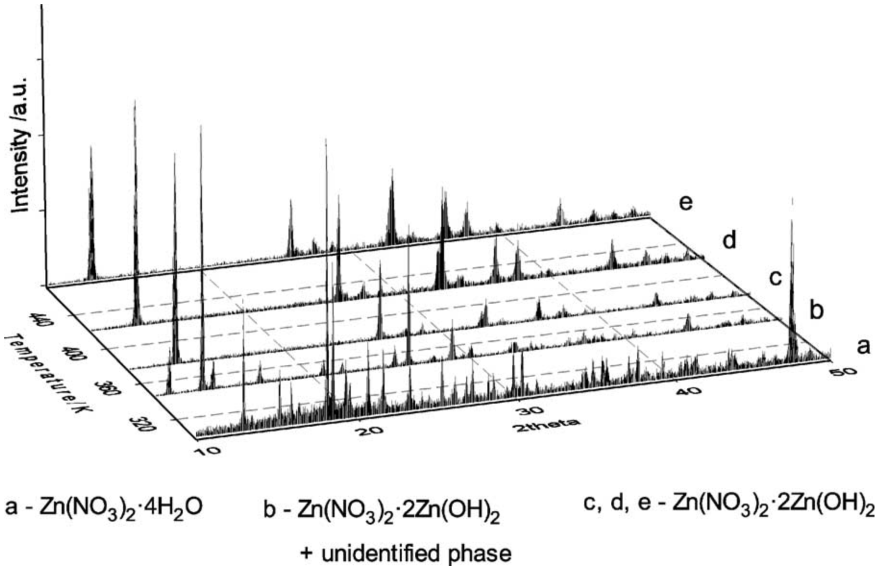

Fig. 6. X-ray diffraction pattern of intermediates of zinc nitrate(V) tetrahydrate decomposition in high-temperature camera (heating rate: 2 K min^{-1}).

to about 480 K. Some other phase was detected at 340 K but its X-ray pattern did not match any zinc–nitrogen–oxygen containing compound. Above 480 K no crystalline phase was found which suggests that the sample is amorphous. The final product of decomposition ZnO in form of fine powder is not seen in XRD analysis.

4. Summary

Few general conclusions on the zinc nitrate(V) hydrates decomposition process can be proposed:

- The stable hydrate $Zn(NO_3)_2{\cdot}4H_2O$ is formed during a quasi-static decomposition of $Zn(NO_3)_2{\cdot}6H_2O$ in dry air. As intermediate crystalline $Zn(NO_3)_2{\cdot}2Zn(OH)_2$ was obtained.
- Degradation of nitrate(V) groups starts when 50–80% (depending on heating rate) hydration water is removed from the system.
- During decomposition performed by continuous heating in helium no pure single stable phase as intermediate product was observed but $Zn(NO_3)_2{\cdot}2Zn(OH)_2$ was found to be one of the solid components of reacting mixture.
- In the very last stage of decomposition, no mass spectral signal of H_2O was found which suggests the presence of anhydrous $Zn(NO_3)_2$.
- A considerable shift of the final temperature of decomposition of about 100 K is observed while the heating rate rises from 0.25 to 5 K min^{-1}.

Acknowledgements

Authors wish to acknowledge Polish Committee for Scientific Research for financial support of this work under project no. 11.11.160.94.

References

[1] M. Izaki, J. Katayama, J. Electrochem. Soc. 147 (2000) 210.
[2] Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards (Circular no. 500), Washington, DC, 1952.
[3] J.C. Bailer (Ed.), Comprehensive Inorganic Chemistry, vol. 3, Pergamon Press, New York, 1973, p. 237.
[4] A. Ferrari, A. Braibanti, A.M.M. Lanfredi, A. Tiripicchio, Acta Crystallogr. 22 (1967) 240.
[5] B. Ribar, W. Nowacki, M. Sljukic, F. Gabela, B. Matkovic, Z. Kristallogr. 131 (1970) 175.

[6] D. Popov, R. Herak, N. Radulovic, B. Ribar, Z. Kristallogr. 142 (1975) 347.

[7] D. Weigel, B. Imelik, M. Pretrre, Bull. Soc. Chim. 4 (1964) 836.

[8] G. Pannetier, G. Djéga-Maraidassou, C. R. Acad. Sci. Paris 261 (1965) 3146.

[9] M. Louër, D. Louër, D. Weigel, C. R. Acad. Sci. Paris 270 (1970) 881.

[10] M. Louër, D. Louër, D. Weigel, C. R. Acad. Sci. Paris 266 (1968) 59.

[11] W. Feitknecht, Fortschr. Chem. Forsch. 2 (1953) 670.

[12] M. Louër, D. Louër, D. Grandjean, Acta Crystallogr. B29 (1973) 1696.

[13] Wiley Registry of Mass Spectral Data, sixth ed., Wiley, New York, 1994.