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Thermal decomposition of cadmium formate in inert and oxidative atmosphere

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ABSTRACT

Thermal decomposition of cadmium formate, $Cd(HCOO)_2$, was studied in dynamic helium and air atmosphere by means of simultaneous TGA, DTA and MS analysis. It was found that the cadmium formate decomposes at about 210 °C to metallic cadmium and cadmium carbonate which next decomposes with formation of cadmium oxide. In helium cadmium melts, evaporates and the reaction residue consists of CdO and a small amount of elementary carbon formed in result of pyrolysis of formate groups. In air cadmium oxidizes and the final solid product of decomposition is CdO. The gaseous products of cadmium formate decomposition are: carbon dioxide, water, carbon monoxide, formaldehyde, methyl alcohol and methyl formate.

1. Introduction

Cadmium and its compounds find a wide spectrum of technological applications in industry and analysis as catalysts, colorants, elements of sensors and storage batteries (nickel–cadmium or silver–cadmium), stabilizers, materials for semiconductors and transparent conductive oxide films [1–9]. Authors of the present paper in recent years made an effort to study thermal decomposition of the series of cadmium carboxylates and dicarboxylates (cadmium malonate, acetate and succinate) to reveal the individual role of the cation and the anions in this reaction [10–12]. This work concerns the decomposition of cadmium formate in inert and oxidative atmosphere.

The anhydrous cadmium formate has a monoclinic, polymer structure with seven-coordinated Cd atoms with the distorted square-pyramidal geometry. Each cadmium atom is combined with seven oxygen atoms belonging to five different formic ligands [13]. It means that in the cadmium formate structure there are bridging and chelating Cd–O bonds with length in the range 2.259(4)–2.599(7) Å.

The reaction of thermal decomposition of $Cd(HCOO)_2$ was not investigated very often earlier. In paper [14] which was devoted to the decomposition in inert atmosphere of series of metal formates the metallic cadmium and cadmium carbonate were indicated as products of $Cd(HCOO)_2$ decomposition. As a main gaseous product CO_2 was reported and little amounts of CO, methyl alcohol and methyl formate.

Thermal decomposition of cadmium formate was studied on the occasion of research on the hydrated mixed Cu–Cd formats [15] and Sr–Cd formats [16] in oxidative atmosphere. As solid intermediate products anhydrous formates were reported. For decomposition of $CdSr(HCOO)_4$ the final product was mixture of CdO and $SrCO_3$ and decomposition of $Cu_{0.47}Cd_{0.53}(HCOO)_2$ lead to mixture of CdO and CuO.

The goal of this work is to find out the routes of decomposition of cadmium formate as well as solid and gaseous products of this reaction.

2. Experimental

2.1. Material

Cadmium formate was synthesized by dissolving cadmium carbonate in a hot, 15% aqueous solution of formic acid. According to high volatility of formic acid 10% excess of this reactant was used. All reactants were analytically pure and delivered by P.O.Ch. Gliwice S.A. The received solution was filtered off and left for a period of 4–5 weeks for the crystallisation process. The crystals formed were washed with distilled water, filtered using Büchner's funnel to remove the remaining formic acid and then dried at 130 °C in a dryer to receive an anhydrous compound. After grinding in an agate mortar, the fraction of 10–100 μm grain size was separated for further investigations. The sample was kept in a desiccator over CaO during the whole process of investigations.

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2.2. Methods

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on SDT 2960 TA INSTRUMENTS apparatus. The samples of mass around 10 mg were placed in the standard platinum crucibles and heated at rates between 2 °C min^{-1}, 5 °C min^{-1} and 10 °C min^{-1}. All presented results were obtained at heating rate: 5 °C min^{-1}. The measurements were carried out under dynamic conditions (the flow of 100 cm^3 min^{-1}) in helium (purity 99.999%) and synthetic air atmospheres (<15 ppm H_2O).

The volatile products of decomposition were analysed using the quadrupole mass spectrometer BALZERS QMD 300 THERMOSTAR operated with an electron impact ionizer (70 eV). The mass spectrometer was connected on-line with SDT apparatus by the quartz capillary heated up to 200 °C. The measurements were performed in a scan mode for m/z (where m is mass of the molecule and z is a charge of the molecule in electron charge units) range from 10 to 114, which is the atomic weight of cadmium isotope ^{114}Cd.

The amounts of carbon and hydrogen in the prepared reactant were measured using combustion analysis. Cadmium content was determined using atomic absorption spectroscopy. The phase composition of the initial sample, samples decomposed to some extent and solid residue was carried out using Phillips X-ray diffractometer using CuKα radiation. IR spectroscopy of the reactants was performed on BIO-RAD FTS60V spectrometer using the KBr pellet technique. The residue was also analysed by JMS-5400 (JEOL) scanning electron microscope.

3. Results and discussion

The chemical composition of the initial sample was determined as: 55.6% Cd (55.53%), 11.6% C (11.87), 0.9% H (1.00%) and agreed well with theoretical expectation for an anhydrous cadmium formate (in brackets). The chemical analysis was supplemented with X-ray diffraction analysis and infrared spectroscopy. The X-ray pattern for the powder received differs from data in ASTM card *ICDD 32-1357* for $Cd(HCOO)_2$ (Fig. 1), but this card is described as "doubtful" in database. IR spectrum of initial sample having signals at 2958 cm^{-1}, 2920 cm^{-1}, 2865 cm^{-1}, 2747 cm^{-1}, 2715 cm^{-1}, 1603 cm^{-1}, 1572 cm^{-1}, 1405 cm^{-1}, 1380 cm^{-1}, 1358 cm^{-1}, 1064 cm^{-1}, and 764 cm^{-1} corresponds with the results published earlier [17].

3.1. Decomposition in helium

The thermal decomposition of $Cd(HCOO)_2$ in helium starts approximately at about 210 °C (DTG onset). On the TG curve three steps are seen (Fig. 2) in the temperature ranges: 210–300 °C (1st stage), 300–340 °C (2nd stage) and 340–600 °C (3rd stage). The total mass loss to the end of the process is about 75% at the heating rate 2 °C min^{-1} to 85% at the heating rate 10 °C min^{-1} and is much higher than theoretical weight loss equal to 36.57% when assuming CdO as the final product or 44.47% when assuming Cd as the final product of decomposition. This means that the mass loss is connected with the evolution of the volatile products which have to arise not only from decomposition of formate groups but also have to contain cadmium.

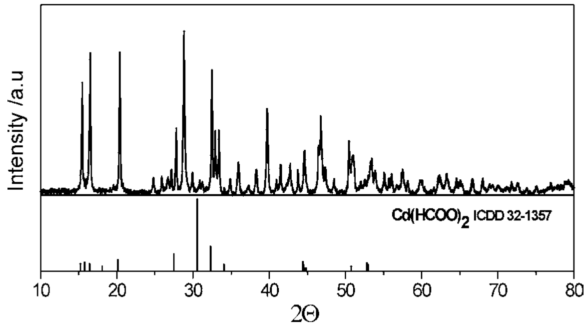

Fig. 1. XRD pattern of synthesized $Cd(HCOO)_2$ and spectrum of $Cd(HCOO)_2$ form ASTM card *ICDD* 32-1357.

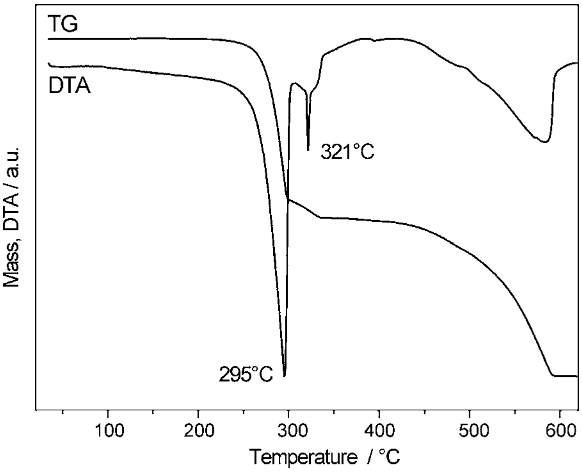

Fig. 2. TG and DTA curves of $Cd(HCOO)_2$ decomposition in helium (5 °C min^{-1}).

The results of XRD analysis of the sample taken from 285 °C presented in Fig. 3 show that in the 1st stage Cd, $CdCO_3$ and CdO form. The presence of $CdCO_3$ in this sample was additionally confirmed by IR spectroscopy but the IR spectrum was distorted by cadmium oxide and traces of elementary carbon. This stage of reaction is connected with the mass loss about 37% and strong single endothermic effect on the DTA curve.

After the 2nd stage of decomposition in the sample Cd and CdO was found. In this stage two overlapping endothermic peaks on the DTA curve are seen: one corresponding to decomposition of $CdCO_3$ and the second, very sharp peak at 321 °C, corresponding to cadmium melting [18]. The mass loss is about 4.0%.

The partial pressure of cadmium increases from about 14 Pa at 321 °C to 9 kPa at 600 °C (calculated on the basis of thermodynamic data from [19]) which means that cadmium evaporates and the 3rd stage of mass loss on the TG curve is connected with this process. The residue at 600 °C was CdO (Fig. 3). EDS analysis of the residue revealed also the traces of carbon (Fig. 4). Elementary car-

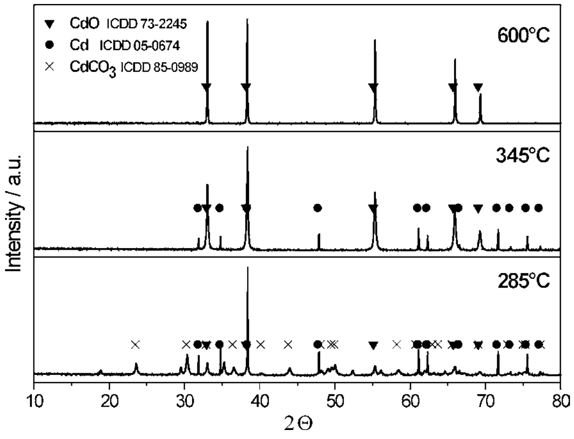

Fig. 3. XRD patterns of samples of partially decomposed $Cd(HCOO)_2$ taken from different temperatures (helium).

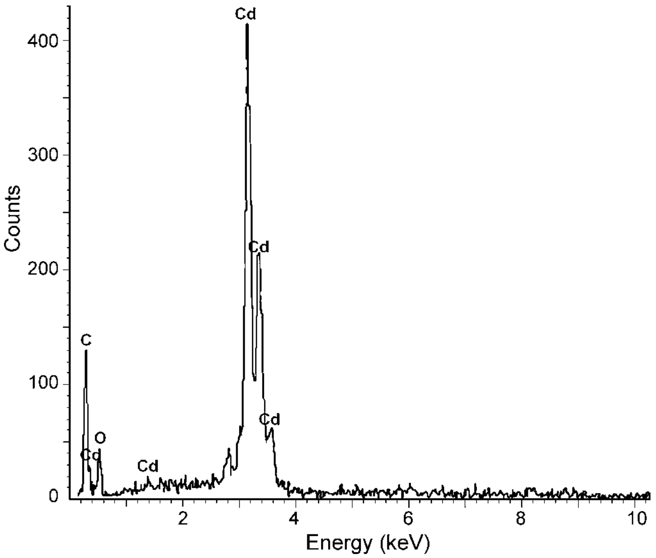

Fig. 4. EDS analysis of the residue of $Cd(HCOO)_2$ decomposition in helium.

bon is produced in result of pyrolysis of formate groups. The mass loss in the 3rd stage is about 40% for the measurement carried out at 5 °C min^{-1} and presented in Fig. 3, but reaches about 44% during measurement at 10 °C min^{-1}. This difference can be explained taking into consideration that at the 3rd stage cadmium is partly oxidized by the traces of oxygen present in helium. The longer time of the experiment at the low heating rate makes the oxidizing advances and leads to the lower mass loss.

The mass spectrum of the gas produced by the decomposing cadmium formate in the 1st stage of decomposition contained the following m/z signals: 12, 15, 16, 17, 18, 28, 29, 30, 31, 32, 44 and 60. The analysis of this spectrum showed that in this stage the following gas products evolve: carbon dioxide, water, carbon monoxide, formaldehyde (HCOH), methyl alcohol (CH_3OH) and methyl formate ($HCOOCH_3$). Table 1 contains mass spectra of gaseous products of decomposition taken from NIST database [20]. Fig. 5 shows intensities of detected m/z signals characteristic of the identified gases. From the comparison of the surface area of m/z signals it can be deduced that the main gaseous product of $Cd(HCOO)_2$ thermal decomposition is CO_2.

The only gas evolved during the second stage was CO_2. No evolution of gas was observed for the third stage of decomposition.

Taking into consideration the results of the analysis of solid and gaseous products of reaction in helium it can be stated that decomposition proceeds as follows:

- 1st stage:

$$Cd(HCOO)_2 \rightarrow xCdCO_3 + (1-x)Cd$$
$$+ (CO_2, CO, H_2O, HCOH, CH_3OH, HCOOCH_3)\uparrow$$

Table 1
Mass spectra of the gaseous products of $Cd(HCOO)_2$ decomposition [20]

Compound	Mass spectrum m/z (intensity)
CO_2	44(100), 28(9,8), 16(9,6), 12(8,7), 22(1,0)
H_2O	18(100) 17(21,0) 16(1,0)
CO	28(100) 12(4,7) 16(2,0)
HCOH	29(100) 30(58,0) 28(24,0) 15(2,0) 12(1,0)
CH_3OH	31(100) 32(75,0) 29(44,0) 15(12,0) 30(6,4) 28(4,5)
$HCOOCH_3$	31(100) 32(46,0) 29(45,0) 60(38,0) 15(19,0) 30(6,0) 28(4,8) 44(1,0)

Only signals with intensity >1% were given.

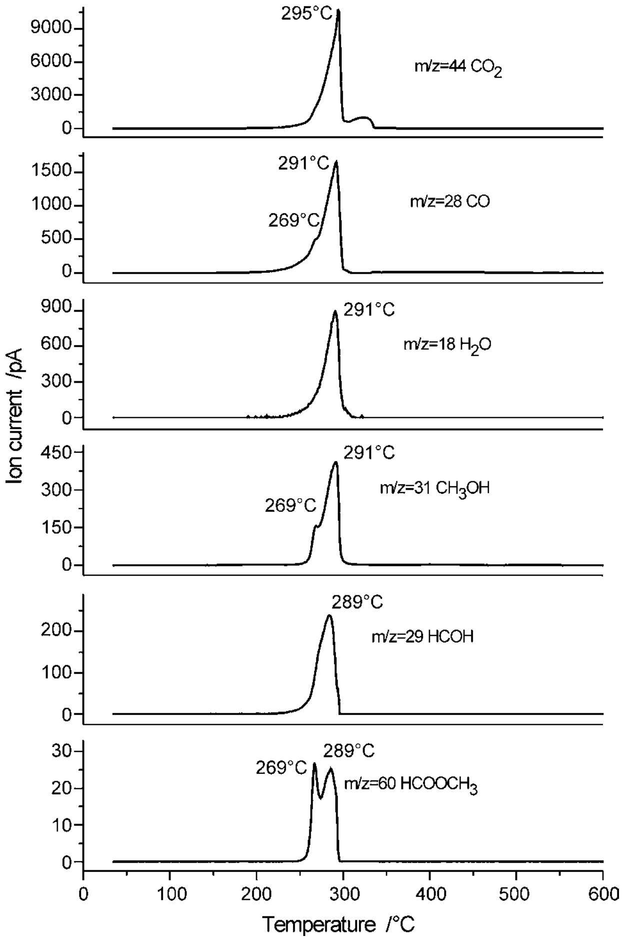

Fig. 5. Mass spectrometric signals of chosen m/z recorded during decomposition of $Cd(HCOO)_2$ in helium.

- 2nd stage:

$$CdCO_3 \rightarrow CdO + CO_2\uparrow$$

- 3rd stage:

$$Cd_{liquid} \rightarrow Cd_{vapour}\uparrow$$

Calculations carried out on the basis of the mass change in the second stage of decomposition as well as the weight of the residue indicated that the value of x for the 1st stage of reaction can be estimated as 0.2–0.3.

3.2. Decomposition in air

The thermal decomposition of cadmium formate in air proceeds by two separate stages (Fig. 6). Average total mass loss of 36.6% in the whole reaction stays in a good agreement with theoretical value 36.57% assuming CdO as the final product of decomposition. The first stage, with the mass loss of 32% within the temperature range 210–290 °C, is accompanied by very strong exothermic effect. XRD pattern of the sample taken from 290 °C reveals signals for CdO and $CdCO_3$ (Fig. 7). The second stage (290–365 °C) is described by endothermic effect on the DTA curve and the mass lost about 7.3% in relation to mass from 290 °C. The XRD pattern for sample at 400 °C (Fig. 7) reveals only the signals of CdO.

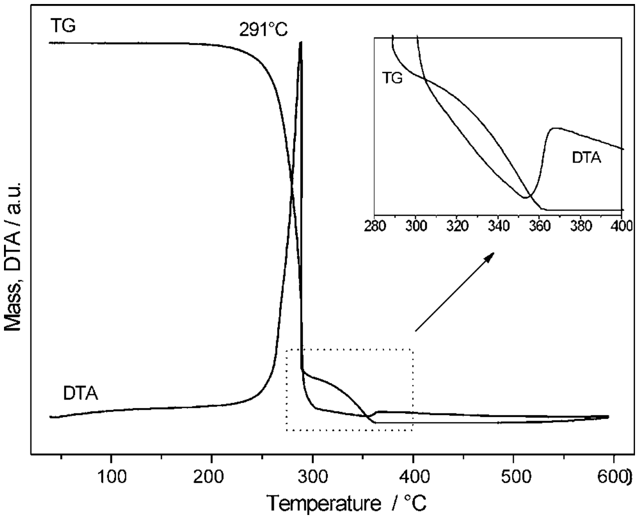

Fig. 6. TG and DTA curves of $Cd(HCOO)_2$ decomposition in air (5 °C min^{-1}).

The mass spectrum of the gas evolving from the decomposing cadmium formate in the first stage contained the same m/z signals as during decomposition in helium: 12, 15, 17, 18, 29, 30, 31 and 44, except of 60. The intensity of signal $m/z = 60$ is about 100 times lowers than that for $m/z = 44$. Based on these results as gaseous products of decomposition in air H_2O, CO_2 and HCOH, CH_3OH, $HCOOCH_3$ can be stated. The changes in intensity of m/z signals 28 as well as 16 and 32 cannot be measured because they occur compared to high-level signals corresponding to N_2 and O_2, respectively, which are components of air. In consequence these important signals characteristic of HCOH and CH_3OH cannot be considered. Some gaseous products like $HCOOCH_3$ can be oxidized in the secondary reactions in which a great amount of CO_2 and H_2O is produced. The lack of signal $m/z = 60$ in the spectrum is probably the consequence of low content of $HCOOCH_3$ in gaseous products ($m/z = 60$ is the fourth highest signal in $HCOOCH_3$ spectrum) resulting from its oxidation.

CO_2 is the only gaseous product emitted above 290 °C in the second stage of decomposition (Fig. 8).

The strong exothermic effect for the first stage of $Cd(HCOO)_2$ decomposition in air, the absence of cadmium in the sample partially decomposed and lack of endothermic effect with the minimum at 321 °C suggest that cadmium (the original product of thermal decomposition of cadmium formate) is oxidized to CdO by the oxygen from air.

In conclusion it was found that cadmium formate thermal decomposition in air proceeds similarly as in helium:

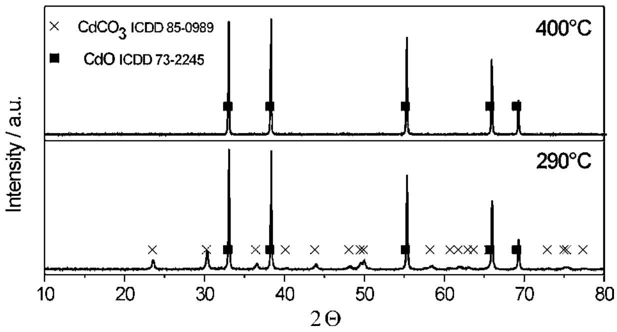

Fig. 7. XRD pattern of partially decomposed $Cd(HCOO)_2$ taken from 290 °C and the final product of decomposition (air).

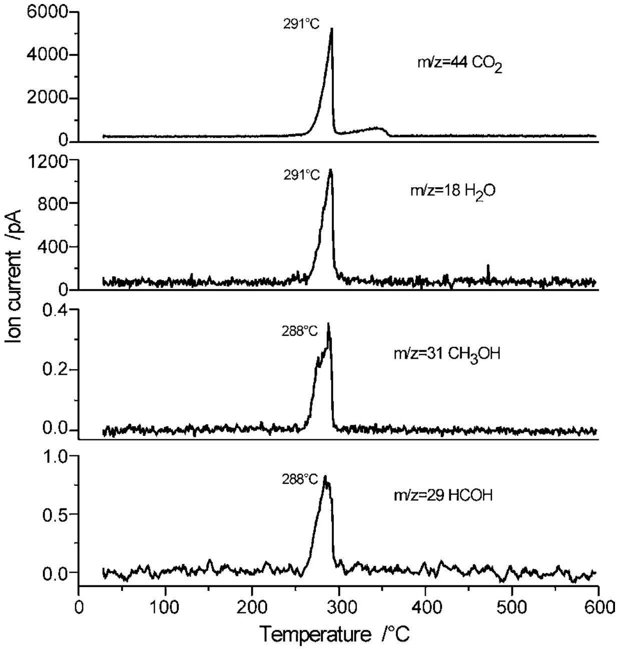

Fig. 8. Mass spectrometric signals of chosen m/z recorded during decomposition of $Cd(HCOO)_2$ in air.

- 1st stage:

$$Cd(HCOO)_2 \rightarrow xCdCO_3 + (1-x)Cd + (CO_2, H_2O, HCOH, CH_3OH, HCOOCH_3)$$

$$Cd + 1/2O_2 \rightarrow CdO$$

- 2nd stage:

$$CdCO_3 \rightarrow CdO + CO_2$$

The x value calculated in the same way as it was done for reaction in helium was found to be 0.2–0.3 which is the same range as for the decomposition in helium.

4. Summary

The temperature of the beginning of decomposition of cadmium formate which is 210 °C is not influenced by the gas atmosphere. This can be regarded as the argument that the mechanism of reaction is the same in inert and oxidative environment.

The decomposition proceeds in two stages. The first stage leads to the cadmium and cadmium carbonate as the solid products. In inert atmosphere cadmium melts and evaporates. The rate of cadmium evaporation is significantly high when the temperature exceeds 400 °C. In oxygen containing atmosphere cadmium immediately oxidizes to CdO.

The temperature of the second stage is 300 °C. In this stage $CdCO_3$ decomposes to CdO with evolution of CO_2 as the only gaseous product. In result the residue of $Cd(HCOO)_2$ decomposition is CdO, which is the product of $CdCO_3$ decomposition, and in air it is additionally formed as the product of cadmium oxidation being the secondary reaction.

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References

[1] R. Mishra, S.R. Bharadwaj, D. Das, J. Therm. Anal. Calorim. 86 (2006) 547.
[2] N.V. Deshmukh, J. Electron. Mater. 36 (2007) 634.
[3] R.A. Ismail, B.G. Rasheed, E.T. Salm, M. Al-Hadethy, J. Mater. Sci.: Mater. Electron. 18 (2007) 1027.
[4] R. Ferro, J. Rodriguez, Sol. Energy Mater. Sol. Cells 64 (2000) 363.
[5] M.M. Ardakani, A. Dastanpour, M. Salavati-Niasari, Microchim. Acta 150 (2005) 67.
[6] Yu.G. Mourzina, M.J. Schöning, J. Schubert, W. Zander, A.V. Legin, Yu.G. Vlasov, H. Lüth, Anal. Chim. Acta 433 (2001) 103.
[7] P.A. Tikhonov, A.T. Nakusov, I.A. Drozdova, Glass Phys. Chem. 30 (2004) 101.
[8] N.M. Barbin, J. Appl. Electrochem. 36 (2006) 723.
[9] L.N. Kulikova, M.A. Volgin, A.L. L'vov, Russ. J. Electrochem. 41 (2005) 620.
[10] B. Małecka, J. Therm. Anal. Calorim. 78 (2004) 535.
[11] B. Małecka, A. Łącz, A. Małecki, J. Anal. Appl. Pyrol. 80 (2007) 126.
[12] B. Małecka, A. Łącz, J. Therm. Anal. Calorim. 88 (2007) 295.
[13] G. Weber, Acta Crystallogr. B 36 (1980) 1947.
[14] A. Górski, A. Kraśnicka, J. Therm. Anal. 32 (1987) 1243.
[15] A.G. Leyva, G. Polla, D. Vega, R. Baggio, P.K. de Perazzo, M.A.R. de Banyacar, M.T. Garland, J. Solid State Chem. 157 (2001) 23.
[16] V.Z. Vassileva, Thermochim. Acta 298 (1997) 135.
[17] A. Sunila, G. Aruldhas, Spectrochim. Acta 51A (1995) 79.
[18] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 13th ed., McGraw-Hill Book Co., New York, 1985.
[19] K. Barbalace, Chemical Database, EnvironmentalChemistry.com, 1995–2008.
[20] NIST Standard Reference Database, 69, June 2005 Release.