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Research Note

Thermal Behavior of Alkaline Lead Acetate, a Study of Thermogravimetry and Differential Scanning Calorimetry

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The compound, alkaline lead acetate, $Pb(CH_3COO)_2{\cdot}PbO{\cdot}H_2O$ (ALA), was purchased from the Fluka Company. The X-ray diffraction film and SEM electron micrograph of this compound were obtained and reported in this paper for the first time. The thermal behavior of alkaline lead acetate (ALA) was studied using thermogravimetery (TGA) and Differential Scanning Calorimetery (DSC) techniques under an O_2 gas atmosphere from 25 to 600°C. Four distinct energy changes associated with weight changes were observed, all of them being exothermic in the DSC results. The amount of ΔH for each peak is reported.

INTRODUCTION

Lead metal and its compounds have been studied and reported in [1-6]. The preparation of Alkaline Lead Acetate has been reported by a number of researchers, and different chemical compositions have been identified and reported [7,8]. The chemical formula of their products has been influenced by their preparation methods and techniques. The existence of $Pb_2(OH)_2(CH_3COO)_2$ was confirmed by UV investigations and elemental analysis [9]. The stoichiometric formula $Pb(CH_3COO)_2{\cdot}PbO{\cdot}H_2O$ was also confirmed by elemental analysis [10].

The goal of this work was to obtain the X-ray diffraction pattern of the alkaline lead acetate $Pb(CH_3COO)_2{\cdot}PbO{\cdot}H_2O$, purchased from the Fluka Co., with a supplied elemental analysis, with no X-ray diffraction data reported in the literature. Also, to study the thermal behavior of alkaline lead acetate (25 - 600°C) for the first time and report the thermodynamic values of thermal decomposition stages were observed in Differential Scanning Calorimetry experiments. The texture of this material was studied by using a scanning electron microscope.

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EXPERIMENTAL

Materials and Equipment

Alkaline Lead Acetate (ALA) was purchased from the Fluka Co., Switzerland; article no. 15317.

TGA:	Thermogravimeter, Mettler TG50 coupled with a TA processor;
XRD:	X-ray diffractometer D 5000, Siemens, Kristalloflex;
SEM:	Scanning electron microscope, REM-JEOL (GSM-840).

X-RAY DIFFRACTION OF ALKALINE LEAD ACETATE

The starting material, as well as the products, were finely ground and prepared on a sample holder using Scotch tape and Bedacryl I.C.I. They were X-rayed with CuKα1 radiation for two hours, using a Guinier camera with focusing quartz monochromators (see Table 1 and Figure 1).

ELECTRON MICROSCOPIC INVESTIGATION OF ALKALINE LEAD ACETATE

The preparation of the sample was accomplished by gold coating its surface for 3-4 min. The morphologic

Table 1. XRD lines of ALA.

No.	d	I[a]	No.	d	I[a]
1	12.18	Vs	27	2.34	w
2	10.21	M	28	2.31	w
3	7.96	S	29	2.23	m
4	7.59	M	30	2.16	w
5	6.68	S	31	2.13	m
6	6.10	W	32	2.03	m
7	5.21	Vw	33	1.91	m
8	4.49	S	34	1.89	w
9	3.74	Vs	35	1.88	w
10	3.48	M	36	1.84	w
11	3.42	M	37	1.81	w
12	3.35	M	38	1.76	m
13	3.29	M	39	1.73	w
14	3.17	M	40	1.68	m
15	3.04	Vs	41	1.65	m
16	2.95	M	42	1.60	w
17	2.88	M	43	1.56	w
18	2.84	W	44	1.53	w
19	2.79	W	45	1.51	w
20	2.75	W	46	1.48	w
21	2.71	W	47	1.42	w
22	2.67	W	48	1.39	w
23	2.59	W	49	1.36	w
24	2.49	W	50	1.33	w
25	2.43	S	51	1.28	w
26	2.40	W	52	1.26	w

a) v: very; s: strong; m: medium; w: weak.

investigation of the ALA sample was accomplished on a SEM (REM-JEOL-JSM-840) instrument. The reasonable enlargements were 1000 times and the final micrograph is shown in Figure 2.

THERMAL STUDIES OF ALKALINE LEAD ACETATE

TGA Analysis of ALA

A standard crucible (from corundum) was filled with 46.947 mg ALA and placed into the TG balance (Mettler-TG 50 with a TA processor attached). The sample was heated (heating rate of 1°C/min) under a stream of O_2 gas (flow rate of 15 ml/min) from 25°C to 600°C. The weight of this sample was recorded during the heating process and TG curves are shown in Figures 3 to 5.

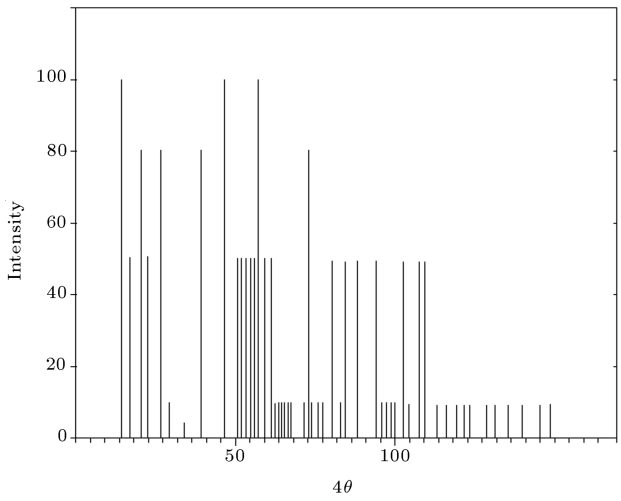

Figure 1. XRD diagram of alkaline lead acetate.

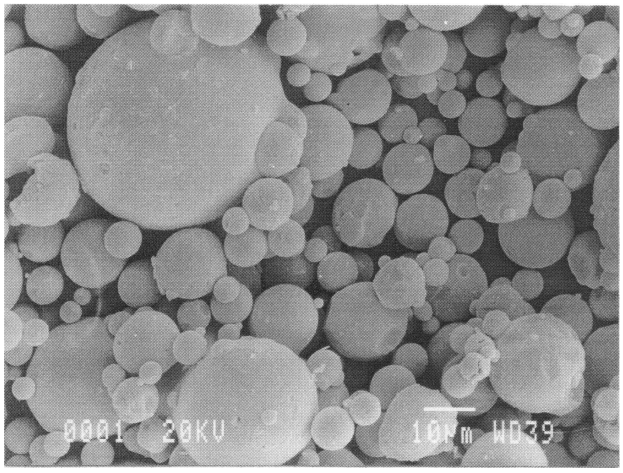

Figure 2. SEM electron microscopic photograph of alkaline lead acetate, enlargement is 1000 X.

DSC Analysis of ALA

36.861 mg of an ALA sample were placed in a standard aluminum crucible and sealed with special equipment. The sealed sample was placed in the DSC equipment and heated from 25 to 600°C, with a heating rate of 1°C/min under an O_2 gas atmosphere. The DSC curve of this sample is shown in Figure 6.

RESULTS AND DISCUSSION

The X-ray diffraction data of the ALA sample is obtained and reported in Table 1. The ASTM (American Society for Testing and Materials-XRD) diagram for ALA has not been reported in the references. Therefore, the XRD diagram of ALA shown in Figure 1 has been prepared by using data obtained in this work for the first time.

A SEM photograph of alkaline lead acetate is

shown in Figure 2, where large round particles with diameters of 1-45 μm are observed.

A simple TG curve of ALA is shown in Figure 3. Five stages are observed in the course of the thermal decomposition. The first three stages are associated with a loss of weight and the fourth stage shows a weight gain followed by a weight loss. The calculations of weight changes are shown in Figure 4. The first weight loss of about 2.5% starts at 100°C and ends at 220°C. The second weight loss of about 6.2% starts at 240°C and ends at 300°C and the next weight loss of about 11.9% starts at 305°C and ends at 350°C. The total weight loss within the temperature range of 100-350°C, amounts to about 20.6%. The fourth stage starts suddenly at about 355°C and ends at 460°C, with a weight gain of about 1.3%. This phenomenon could be due to the oxidation of lead from the oxygen present in the TGA chamber. In the final stage, a weight loss of about 1.5% was observed within the temperature range of 505-572°C.

X-ray diffraction of the first two intermediates (white powder) produced in the course of thermal decomposition at 230 and 300°C was obtained and compared with reference tables of known materials. These data could not be found in the literature, therefore, the identity of the first two intermediates is unknown and further investigations could be part of future work.

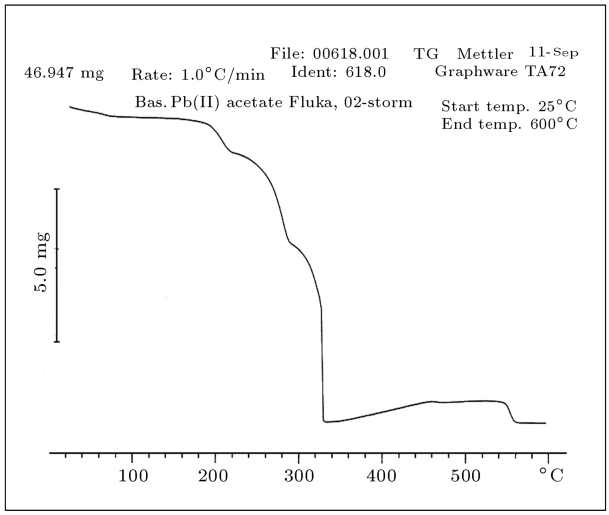

Figure 3. Thermogram of alkaline lead acetate; temperature range 25-600°C, O_2.

A similar procedure was followed for the third intermediate product collected at 360°C. Round metal particles in a yellowish powder are observed and a comparison of XRD data with standard ASTM diagrams confirms the presence of metallic lead, as well as lead oxide (α-PbO and β-PbO) in this sample.

X-ray diffraction of the final product of thermal decomposition at 600°C (a yellow-orange powder) was also obtained. It confirms the presence of a mixture of α-PbO and β-PbO. The chemical analysis [11,12] showed no impurities. Table 2 shows the results of the thermal decomposition of ALA in a temperature range of 25-600°C.

Both TG and DTG curves of ALA are shown in Figure 5. A comparison of the two curves would help an understanding of the rate of weight loss at each stage and provide more information about rates of decomposition at each stage and possible interaction between two consecutive stages.

The DSC curve of ALA, in the temperature range of 25-600°C, is obtained and shown in Figure 6. Four distinct peaks are observed within the temperature range of 180-420°C, with a very small peak as the fifth one at the final stage. All reactions are exothermic. A TA processor was employed to obtain ΔH values for each peak using an integration method. DSC data are summarized and reported in Table 3.

The first peak starts at 185°C, having a maximum point at 228.5°C and ending at 240°C with a calculated ΔH value of 147.0 J/g, which is equal to 83.26 kJ/mol. The second peak starts at 240°C, having a maximum point at 293.4°C and ending at 310°C with a calculated ΔH value of 438.5 J/g, which is equal to 248.4 kJ/mol. The third peak starts at 312°C, having a maximum point at 350.2°C and ending at 365°C with a calculated ΔH value of 1658 J/g, which is equal to 939.1 kJ/mol.

The fourth peak starts at 372°C, having a maximum point at 391.6°C and ending at 422°C with a

Table 2. Results from the TGA curve of ALA in temperature range of 25-600°C in O_2 atmosphere.

Stage No.	Start Temp. (°C)	Turning-Point (°C)	End Temp. (°C)	Weight Decrease	
				mg	%
1	100	207	220	-1.20	-2.55
2	240	279	300	-2.91	-6.19
3	305	327	350	-5.59	-11.91
4	355	407	460	+0.62	+1.32
5	505	555	572	-0.71	-1.52

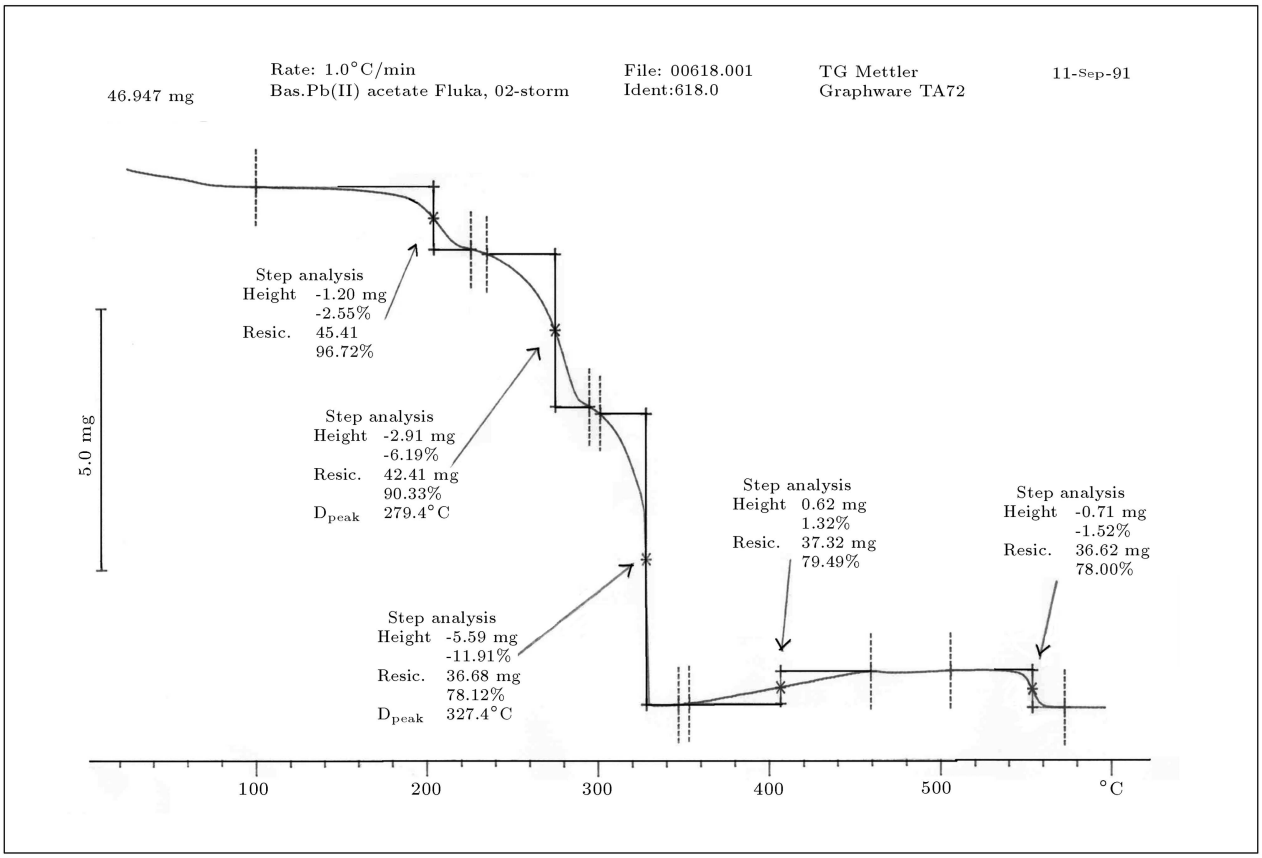

Figure 4. Thermogram of alkaline lead acetate; temperature range 25-600°C, O_2.

Table 3. Results from the DSC curve of ALA in temperature range of 25-600°C in O_2 atmosphere.

Stage No.	Start Temp. (°C)	Turning Point (°C)	End Temp. (°C)	ΔH	
				mJ	J/g
1	185	228.5	240	5417	147.0
2	240	293.4	310	16164	438.5
3	312	350.2	365	61115	1658.0
4	372	391.6	422	3628	98.4

calculated ΔH value of 98.4 J/g, which is equal to 55.7 kJ/mol.

DSC and TGA data confirms the same pathway for decomposition, with a close agreement on temperature considering capabilities of each technique.

CONCLUSION

X-ray diffraction patterns of the starting material, intermediates and final product have been obtained. These films have been compared with the data of standard known lead compounds. No references to starting material could be found in the literature, so it is the first time it has been reported in this paper. X-ray data of intermediate stages were obtained. Even though they are not mixtures of known materials, a suitable match in comparison with the known reported compounds could not be found. However, the obtained X-ray data of the final product corresponds to that of α- & β-PbO reported in a standard reference (ASTM 38-1477 & ASTM 5-561).

The thermal decomposition of ALA (between 25 - 600°C) has been studied by TGA and DCS techniques. The starting material, ALA, undergoes several stages of thermal decomposition, ending with the final product of PbO at 600°C. TGA and DSC curves confirm the existence of these stages.

The enthalpy values were calculated by integra-

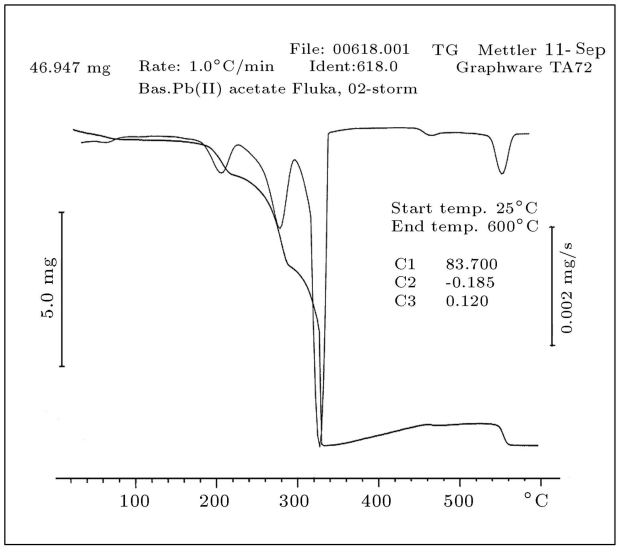

Figure 5. Thermogram of alkaline lead acetate; TG and DTG curves; temperature range 25-600°C, O_2.

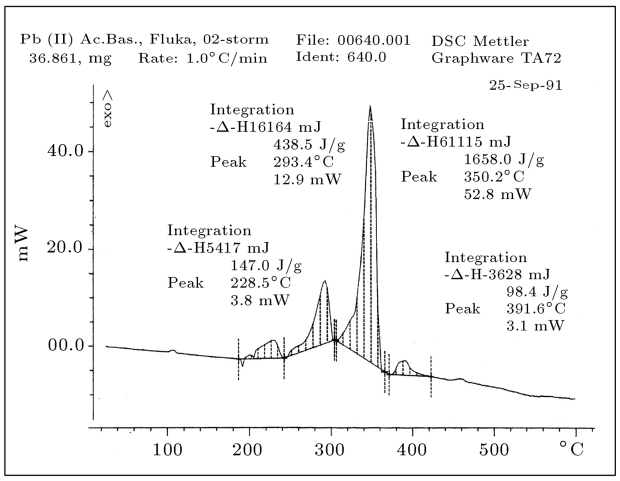

Figure 6. DSC diagram of alkaline lead acetate; temperature range 25-600°C, O_2.

tion of the area for each peak in the DSC curve and are reported in Table 3. Future studies are suggested to include identification of the exact chemical formula of intermediate products, as well as obtaining their X-ray diffraction patterns.

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