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DATA ACQUISITION FROM A DIFFERENTIAL THERMAL MICROANALYZER WITH A LOW-COST MICROCOMPUTER

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ABSTRACT

Software has been developed to collect and analyze data from a differential thermal microanalyzer using an Apple II+ microcomputer. This software is composed of different modules which are independent from each other in order to permit their use with various analog-to-digital converters with few modifications. This configuration allows addition of new modules or updating of existing modules with greater ease. The data acquisition during an experiment can be as high as 6000 numerical values in addition to real-time plotting of the thermogram on the screen. The applicability of the software is shown for the characterization of the thermal behavior of a $PbO \cdot SiO_2$ glass.

INTRODUCTION

Differential thermal analysis (DTA) has been used with success for many years to study temperature-dependent transitions in various types of samples. Since this technique was introduced many years ago, many thermal analyzers were bought before the development of dedicated laboratory computers. Today, these instruments are still functional in laboratories and their continued excellent performance does not justify the acquisition of a new computerized DTA system. However, as these thermal analyzers are not computer-controlled, they do not have the flexibility of dedicated-hardware-oriented DTA instruments.

Traditionally, thermal curves were traced with a potentiometric pen recorder. The digitization of the DTA output signal permits the permanent storage of raw data on magnetic supports and, subsequently, the manipulation of data such as plotting of the thermogram, determination of enthalpy or baseline correction. These possibilities can be easily obtained by interfacing a DTA instrument to a low-cost microcomputer.

The interfacing of a microcomputer to an analytical instrument requires a complete knowledge of (i) the analog signal output generated by the instrument; (ii) the capability of the analog-to-digital (A/D) converter and (iii)

the computer system treating the data. For example, with a highly sensitive differential thermal microanalyzer, the analog-to-digital conversion must be sufficiently accurate to transform an analog output in the μV range to its digitized counterpart without loss of precision. The data sampling rate and signal conversion must be done at relatively high speed so as to obtain a detailed thermogram.

In the conception of the software, the first requirement was the visualization of the thermogram on the screen (real-time plotting) during the data acquisition to follow the experiment. The microcomputer memory must be large enough to hold the large number of numerical values generated by the thermocouples during a run and to allow a real-time plotting of the thermogram. Ideally, this number should be as high as possible to avoid interpolations between each point on the thermogram and also to detect rapid or small transitions during an experiment. With a low-cost microcomputer, the available memory is often limited (64K for an Apple II +). An additional memory card was added to the computer to overcome this limitation.

We have developed a software package for an Apple II + microcomputer which acquires data from a differential thermal microanalyzer. The analog-to-digital conversion is achieved with a Keithley digital multimeter and binary data are transferred to the microcomputer via an IEEE-488 interface. Once data have been stored, they can be transferred to a more powerful computer such as a VAX-750 to speed up data handling and to take advantage of improved graphical capabilities. Details and performance of these systems will be described in following sections using the crystallization of a lead silicate glass as a typical example.

HARDWARE

DTA instrumentation

A 25-year old differential thermal microanalyzer Model M-1 built by BDL (Bureau de Liaison, Paris, France) was fitted with a semi-micro probe Model GS from SETARAM (7, rue de l'Oratoire, 69300, Caluire, France). The probe head (Mazières type) was made of three platinel II thermocouples located inside a chamber resting on top of a refractory support [1]. Each thermocouple was welded to a platinum crucible (25 μl). The three thermocouples were positioned at 120° relative to each other and equally spaced. Two thermocouples were wired differentially to give the DTA signal between the sample and the reference and the third thermocouple was used for temperature measurement of the DTA chamber. The noise level generated by the probe was around 0.002°C. A temperature difference of one degree yielded a signal of about 40 μV. The oven was controlled by a digital

program controller REX-P100 from RKC Instrument Inc (16-6 Kugahara, 5-Chome, Ohta-ku, Tokyo, Japan).

Data acquisition system

Figure 1 shows a schematic representation of the data acquisition system. A daisy chain configuration was used to connect the microcomputer to the instrument components. A Keithley IEEE-488 scanner Model 705 (Keithley Instruments Inc., 28775 Aurora Road, Cleveland, OH, 44139) fitted with the Model 7059 low voltage scanner plug-in card was used to send sequentially the two analog signals from the probe head of the DTA instrument to the A/D converter. This configuration avoids the use of two A/D converters and allows future additions of other sensors without hardware modifications. The scanner can switch up to ten 2-pole channels in less than 2 ms per channel. The scan rate can be varied through the IEEE-488 bus from 10 ms to 100 s and the scan mode can be continuous or manual.

The analog signal from the two differentially wired thermocouples between the sample and the reference, ΔT, was amplified through a Setaram amplifier Model "bn". The signal of the third thermocouple giving the temperature of the DTA chamber, T, was sent directly to the scanner without amplification. The scanning interval between the two analog signals T and ΔT was set to 0.25 s. This interval was necessary to obtain a stable voltage reading on the digital multimeter serving as the A/D converter.

Analog-to-digital conversion

The Keithley digital multimeter Model 195 was used to read the voltages coming from the scanner and to convert them to digital numbers. The multimeter uses a hybrid A/D converter which uses both charge balance

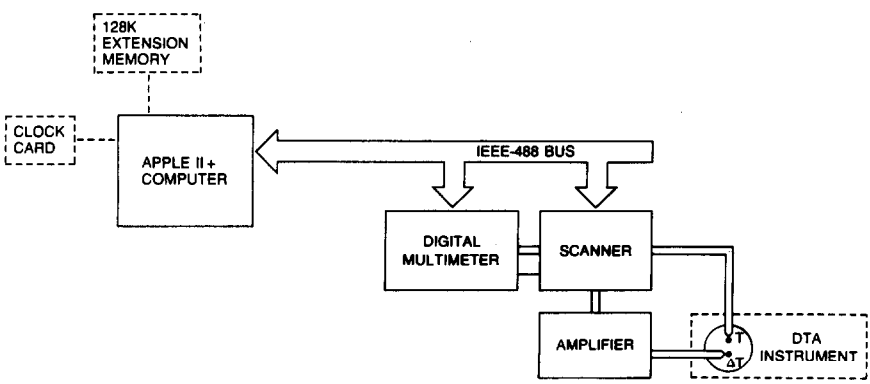

Fig. 1. Schematic representation of the data acquisition system.

and single-slope conversion techniques. The A/D conversion process is controlled by a 6808 microprocessor which supervises all operational aspects of the instrument. The digital multimeter is fully programmable from the microcomputer via the IEEE-488 bus. It is capable of DC voltage measurements between 100 nV and 1000 V on six ranges with a $5\frac{1}{2}$ digit resolution. There is a seventh range, called auto-range, which automatically selects the optimum DC range for maximum precision. In practice, the DC voltage auto-range option is useless for fast data acquisition because the stability of the reading is too low to obtain a reproducible voltage value. For this reason, a fixed range of ± 200 mV was selected. For this range, the multimeter resolution is 1 μV with an integration period of 16.6 ms, which allows a maximum reading rate of 36 readings per second. The resolution of 1 μV corresponds to a resolution of 0.025 °C for the DTA chamber temperature, T. The DTA signal, ΔT, between the sample and the reference is usually amplified 200–2000 times. Since after amplification, this signal cannot exceed ± 200 mV, the possible range of the DTA signal is ± 2.5 °C to 25 °C. The DTA signal resolution corresponding to 1 μV is 1.25×10^{-4} °C for an amplification factor of 200.

Configuration of the computer

A standard Apple II + microcomputer (Apple Computer, 20525 Mariani Avenue, Cupertino, CA, 95014) comes with 64K of random-access-memory (RAM). In order to obtain an adequate data system, specific cards must be added to the computer. The communication of the digital multimeter with the microcomputer was made through an Apple IEEE-488 interface card. This card allows the computer to control or communicate with up to 14 external devices.

The software is designed to accept 6000 values generated by the DTA probe during an experiment. The available RAM (64K) is not sufficiently large to keep in memory all the data values in addition to the software needed to do the real-time plotting of the curve on the screen during the acquisition. Thus, in order to overcome this drawback, a Saturn memory card of 128K RAM was added to the computer and used as a third electronic disk drive. Data cannot be stored directly on a conventional disk drive because at the highest sampling rate (two numerical values per second) a mechanical disk drive is not sufficiently fast to allow data manipulation between the storage of two data points. These data manipulations include the reading of the clock card, the evaluation of the acquisition time with respect to the specified sampling rate, the reading of the two signals ΔT and T, the conversion of voltage values to temperatures, the plotting on the screen and the storage of data. The main advantage of this configuration is that it allows storage of all the data along with simultaneous plotting of the thermogram on the high-resolution graphic page. A 128K Apple IIe com-

puter can be used without the addition of a memory card with minor modifications to the software. Although, it will not be possible to store 6000 values, it will probably be possible to collect about 4000, which is amply sufficient in the majority of applications. Of course, replacement of the 128K memory card by a RAM card of larger capacity will allow the acquisition of more than 6000 values.

A clock card was added to the microcomputer to control the acquisition rate. This card is used instead of the clock included in the scanner because the time given by the latter requires transformation of the format for transfer to the computer; this is laborious and time-consuming. All reports and graphics generated by the software were sent to an Epson LX-80 printer through a Grappler interface card.

SOFTWARE

Language and disk operation system

The software for the data acquisition system was written in Applesoft BASIC. This is an interpreted language and the process time to perform

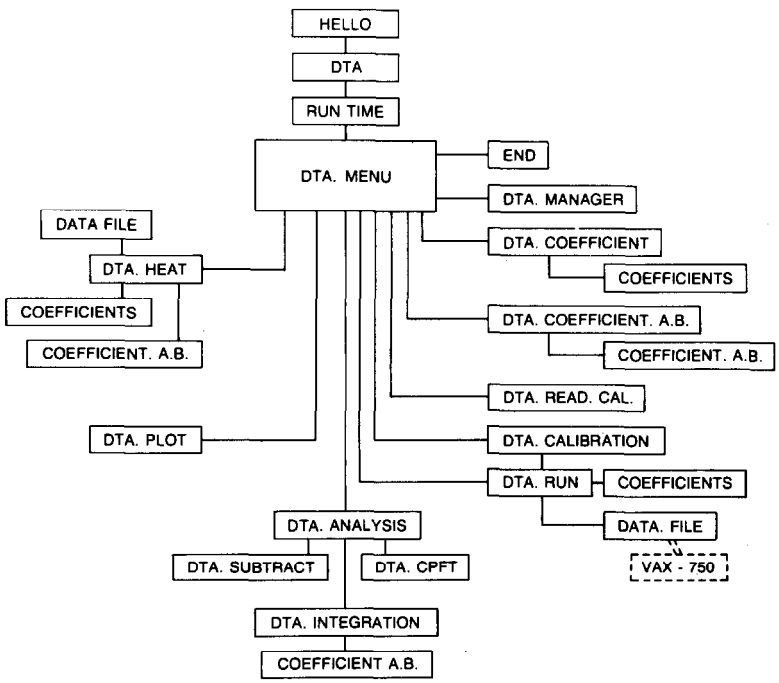

Fig. 2. Schematic representation of the software.

instructions can be relatively long. The real-time plotting of the thermogram requires a rapid treatment of the data coming from the DTA probe. Thus, the software was compiled in binary machine code using the TASC compiler (Microsoft) in order to speed up the process time. The Apple disk operation system (DOS 3.3) was replaced by the Diversi-DOS disk operation system (Diversified Software Research Inc., 34880 Bunker Hill, Farmington, MI, 48018). With Diversi-DOS, the transfer of a data file (text file) from the computer memory to a diskette and vice versa is accelerated by a factor of six in comparison to the Apple DOS. A fast data transfer is essential if the number of collected values is higher than 1000.

The software was designed to be used with two disk drives. The program diskette is continuously kept in disk drive no. 1 and data are stored permanently on the second disk drive at the end of the experiment. The software is menu-driven and all the inputs of the user are protected against possible errors so as to avoid accidental program termination. Moreover, the user always has the opportunity to modify an answer after a wrong initial input. The software has been written in several parts or modules because it is too large to fit completely in the computer memory and because this makes it easier to modify for use with other A/D converters. A schematic representation of the software is shown in Fig. 2 and a brief description of each module is given in the following paragraphs.

Main DTA menu

The greeting program, called HELLO, is automatically loaded when the computer is turned on. It activates the additional memory card (128K) to serve as a pseudo-disk drive which allows rapid storage of data coming from the A/D converter. Afterwards, a presentation page of the software

MENU

(0) EXPERIMENT Te - Tr VS T
(1) EXPERIMENT SPECIFIC HEAT
(2) REPLOTTING OF THE CURVE
(3) DATA ANALYSIS
(4) COEFFICIENTS OF THERMOCOUPLES
(5) COEFFICIENTS A + BT **3
(6) READING OF CALIBRATION FILE
(7) CALIBRATION OF THE PROBE
(8) DISK MANAGEMENT
(9) END OF PROGRAM

PRESS A KEY TO MOVE CURSOR OR
THE REQUIRED NUMBER AND RETURN

Fig. 3. Presentation of the menu (DTA.MENU).

(DTA.PIC) and a special machine-language subroutine (RUNTIME), which is necessary to run TASC compiled programs, are loaded in memory. Thus, the program DTA.MENU is automatically run resulting in a presentation of a menu of all the available modules (Fig. 3). When the program DTA.MENU is run, the first item in the menu is highlighted using inverse video output. An item can be chosen by moving the highlighted cursor with any key or by direct input of the number corresponding to the selected item, and then striking the RETURN key. This program is the central point of the software because it links all the modules together.

A program, called DTA.MANAGER, has been developed to do disk management. This program is useful to delete, rename, lock and unlock a file or to verify the available space on the data diskette. The formatting of a new data diskette is also done with this program.

Calibration of the DTA probe

The DTA probe must be calibrated to obtain quantitative measurements of enthalpy or specific heat. Moreover, the replacement of the probe head by another DTA probe for a specific application can require different calibration parameters. Specific modules have been written to avoid frequent modifications of the software.

There are two text files (COEFFICIENTS and COEFFICIENT.A.B) which are created and managed by two modules: DTA.COEFFICIENT and DTA.COEFFICIENT.A.B. These modules are used to read or store coefficients in the text files. The first text file (COEFFICIENTS) contains the coefficients necessary to compute the signal T and ΔT (in °C) from the corresponding voltages. The second text file contains the coefficients a and b of the relation $K = a + bT^3$, which are necessary for computing a change of enthalpy or specific heat [2].

The proportionality constant K relating the heat flow to the DTA signal, ΔT, must be determined for each probe with a known material. For this purpose, the module DTA.CALIBRATION has been written. After the entry of information concerning the material, the module is linked to the data acquisition software DTA.RUN. At the end of the experiment, the user returns to the module DTA.CALIBRATION to compute the constant and store the data in a specific file. The module DTA.READ.CAL is used to read this calibration file in order to obtain the desired values. The determination of many constants K at different temperatures permits the evaluation of the coefficients a and b of the relation $K = a + bT^3$, which are subsequently used for various calculations.

DTA data acquisition

The data acquisition program DTA.RUN is the main module of the software. A flow chart of the program is given in Fig. 4. The memory map of

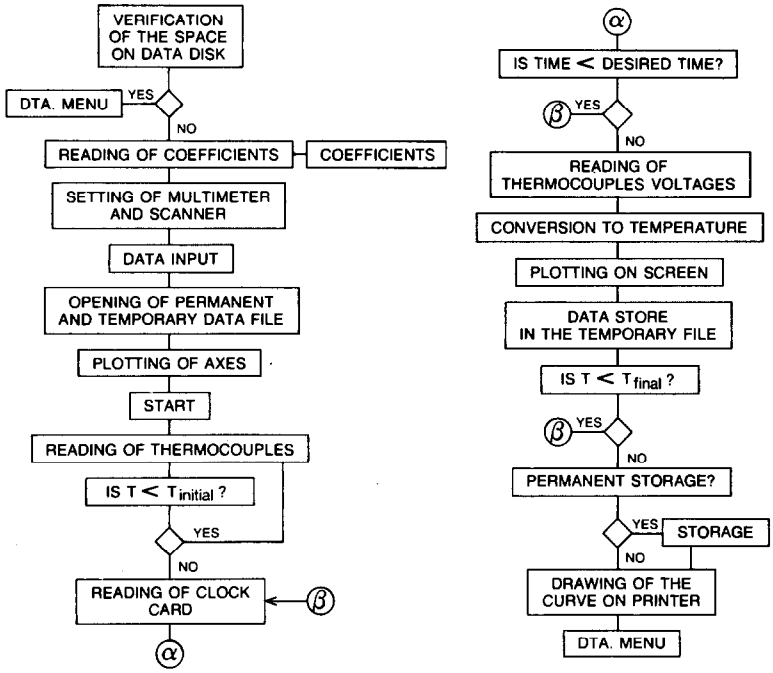

Fig. 4. Flow chart of the module DTA.RUN (data acquisition program).

an Apple II computer is particular since the allowed space for high-resolution graphic page is in the middle of the available memory. As DTA.RUN is a large program, it cannot be run in its interpreted form. The program must be compiled with specific relocation of the binary code in order to optimize the memory usage. The high-resolution graphic page 1 (decimal memory address 8192 to 16383) is employed to have mixed text and graphics on the screen during the acquisition. The shapetable, which is used to produce text characters on the graphic screen, is loaded at memory address 16384. The program itself is stored at the address 18384 and variables are stored at the end of the program. The program RUNTIME which is necessary to run the compiled program is stored between 2051 and 6063.

When the program is run, it first loads the coefficients used in the equation for converting thermocouple voltages to temperature and then initializes the scanner and the multimeter via the IEEE-488 bus. Usual data such as the date, initial and final temperatures, amplification, sample mass, and title are entered in the computer memory and the axes of the graph are drawn on the screen. The resolution, in terms of graphic points (a point is defined as both ΔT and T values), is also required to determine the sampling rate for the acquisition. A maximum number of 3000 points can be entered for the resolution. In many cases, a lower resolution is sufficient and this allows faster subsequent data treatment. The maximum sampling rate

can be 2 values (ΔT and T) per second (a value corresponding to an average of two readings), with a maximum storage of 6000 values. The data acquisition rate is regulated by the clock card. The conversion of the thermocouple voltages to temperature, the storage of data points and the transformation of the data for plotting on the screen require a minimum interval of 1 s between each measurement to read the two voltages. For a heating rate of $10\,°C\ min^{-1}$, a sampling rate of 1 data point per second corresponds to an interval of temperature of 0.17°C, which is sufficient to detect even the fastest transitions.

Before the beginning of the experiment, the program asks the user if there is enough available space on the data diskette to store the data. At this point, it is possible to return to the disk management program to verify the available space. For an experiment using the maximum number of allowable values (6000), it is possible to store only two runs on a 143K diskette. Two modes of storage are used during the experiment. Random access is used to temporarily store data on the memory card. Random text files are more rapidly accessed than sequential text files since the computer does not have to read the entire file from the beginning before writing data. Sequential storage is too slow with long data files, even using a pseudo-disk drive. Thus, random text files are used to store data during the acquisition. However, more space is necessary with random text files. For this reason, when data are transferred permanently to a diskette at the end of an experiment, they are transformed from random access mode to sequential access mode. Data are stored using the ASCII text file format to permit easy transfer to the VAX computer. Files are automatically locked after storage so as to avoid accidental loss of the data.

After the manual start of the oven controller, the computer regularly scans the temperature provided by the thermocouple of the DTA chamber. When this temperature exceeds the chosen initial temperature, the acquisition of data automatically begins at the predetermined sampling rate and the thermogram is simultaneously plotted on the screen as soon as each data point is taken. During the acquisition, it is possible to press the ESC key to obtain three lines of information at the bottom of the screen which show the date, the acquisition time, the number of points taken, the exact values of T and ΔT, and the final temperature. To return to the full page graphic, the user must press the RETURN key.

The acquisition can be stopped at any time by pressing control-F. The user must decide whether to continue the acquisition, store the data permanently, or quit. If the experimental temperature exceeds the selected final temperature, the first option is not allowed. It is also possible to modify the final temperature during the acquisition. The user must press control-T, at which point a question appears at the bottom of the screen asking for a new final temperature. This feature can be used to shorten an experiment or expand it over the initial range of temperature when unforeseen behavior is observed during the experiment.

A second acquisition program, DTA.HEAT, records the specific heat as a function of the temperature. Its logic structure is very similar to the program DTA.RUN.

Data analysis

After the acquisition, the graph is automatically dumped to the printer. However, it is possible to redraw the graph with 5 different configurations as a function of either time or temperature with the program DTA.PLOT. It is also possible to plot on a two y-axis basis to observe the variation of ΔT and the time as a function of the temperature. This is useful to verify whether or not the oven temperature has increased as programmed.

The program DTA.ANALYSIS is a sub-menu which allows the manipulation of data. There is the possibility of (i) subtracting two curves (DTA.SUBTRACT); (ii) integrating the area under the thermogram between two different temperatures (DTA.INTEGRATION) and, (iii) calculating the specific heat for different temperatures (DTA.CPFT). For the subtraction, the processing time is long because the computer has to read two sets of data values, subtract the two curves, keep the results on the electronic disk drive, plot the resulting curve on the screen and on the printer and, if the user wants to keep the subtraction, store the curve permanently on diskette. As an example, it can take about 60 min to perform all these tasks when two curves of 6000 values are subtracted. To reduce this time, data can be transferred to a VAX computer which can accomplish this task in much shorter time.

Data transfer to a VAX computer

Kermit software (public-domain) is used to transfer the data file from the floppy disk to the VAX computer. Once the data have been transferred to the VAX, two programs, written in FORTRAN, are available to perform the subtraction and the transfer of the data file to a file compatible with RS/1 software (BBN Research Systems, 10 Moulton Street, Cambridge, MA, 02238), which is a data analysis system. This software enables the user to manipulate and draw data more easily and more rapidly. There is also the possibility of using the pen plotter, which gives a better resolution than the printer. This makes it easier to detect small variations in the thermogram. The subtraction of two curves on the VAX is achieved in less than one minute, which is a great improvement in comparison with the time needed by the Apple microcomputer.

APPLICATION

It has been shown that additions of small quantities of barium chromate to a glaze containing lead decrease the lead release during leaching in a 4%

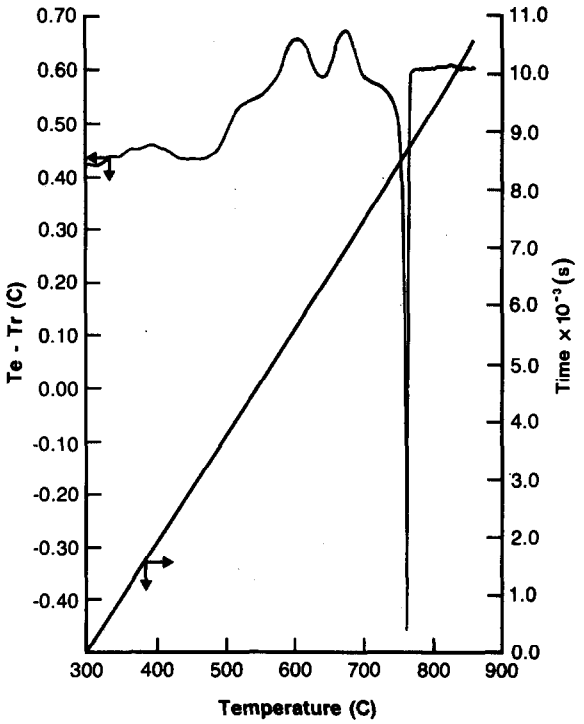

Fig. 5. DTA thermogram of the $PbO \cdot SiO_2$ mixture (1 : 1). Heating rate: 3°C min^{-1}.

acetic acid solution. The decrease depends largely on the thermal history of the glaze [3]. Simple glazes such as $PbO \cdot SiO_2$ have been studied by different techniques including DTA.

A mixture of 1 : 1 $PbO \cdot SiO_2$ was prepared from reagent quality products. The mixture was melted at 1000°C for 1.5 h in a Pt/Rh cup. The melted mixture was poured into a steel mold and annealed at 450°C for 2 h. The disk was ground and the 50 mesh fraction was collected for DTA experiments.

In order to determine the scanning rate which would reveal the most detail, samples were scanned at 1.5, 3.0, and 6.0°C min^{-1}. Both 1.5 and 3.0°C min^{-1} yielded the same results, where three very clearly separated peaks are observed. At 6.0°C min^{-1}, not only were the two exothermic peaks superimposed but the second exothermic peak was truncated by the endothermic peak. It was therefore concluded that the best scan rate was 3.0°C min^{-1}.

The DTA thermogram of the $PbO \cdot SiO_2$ mixture obtained at a heating rate of 3°C min^{-1} is shown in Fig. 5. Three distinct peaks are observed: two exothermic peaks and one endothermic peak. The endothermic peak at 762°C corresponds to the fusion of the thermodynamically stable alamosite $PbSiO_3$ phase [4]. This implies that the glassy sample had undergone

crystallization during the DTA run and hence, the two exothermic peaks must be related to the crystallization of the sample. The increase of the baseline at about 525°C is probably caused by the displacement of the sample in the cup and is not related to a phase transition.

Various authors [4–7] have studied the crystalline species of the $PbO \cdot SiO_2$ system. However, as the experimental conditions used to detect these phases vary greatly, the authors generally disagree as to the domain of the phase transitions as a function of temperature. The three crystalline phases which have been characterized by infrared spectroscopy are: "L-$PbSiO_3$" where "L" reflects that it is stable at low temperatures, a hexagonal phase and finally, a natural phase referred to as alamosite [6].

In order to verify that the two exothermic peaks correspond to a recrystallization, our samples were quenched in air by removing them after the first and the second phase transition. The infrared spectra of these samples show that the first exothermic peak (612°C) corresponds to a glass-hexagonal phase transition whereas the second peak (676°C) represents the phase transition from hexagonal to the alamosite phase. It seems that with our experimental conditions, the "L-$PbSiO_3$" phase is absent.

These thermograms imply that the crystallization sequence in $PbO \cdot SiO_2$ is as follows: glass → hexagonal phase → alamosite and that the alamosite phase cannot be obtained directly from the glassy state. This sequence has not been previously mentioned in the literature.

CONCLUSION

Interfacing of a differential thermal microanalyzer was done with an Apple II + microcomputer. Menu-driven software was written in Applesoft BASIC and then compiled to decrease the process time. With a 128K RAM card acting as a pseudo-disk drive, it is possible to store simultanuously 6000 data values during an experiment and plot in real-time the thermogram on the screen. The software allows a subsequent data treatment such as plotting or integration of the area under the curve. It is also possible to transfer the data file to a VAX computer to speed up some treatments. An example of an application is given for the system $PbO \cdot SiO_2$, where the transformation of the glassy state to the hexagonal phase and subsequently at higher temperature to the alamosite phase is shown.

A copy of the software will gladly be provided if a diskette is sent to the authors.

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