Am. Soc. Metals **44**, 1158–68 (1952).
(4) Flaschen, S. S., Garn, P. D., unpublished measurements.
(5) Garn, P. D., Flaschen, S. S., ANAL. CHEM. **29**, 271 (1957).
(6) Glaser, F. W., *J. Metals* **4**, 391–6 (1952).
(7) Glaser, F. W., Moskowitz, D., *Powder Met. Bull.* **6**, 178–85 (1953).
(8) Glaser, F. W., Moskowitz, D., Post, B., *J. Appl. Phys.* **24**, 731–3 (1953).
(9) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," vol. **VI**, pp. 148, 341, McGraw-Hill, New York, 1929.
(10) Reisman, A., Triebwasser, S., Holtzberg, F., *J. Am. Chem. Soc.* **77**, 4228–30 (1955).
(11) Shimizu, S., *Tohoku Imp. Univ. Sci. Repts.* **22**, 633–61 (1933).
(12) Von Hippel, A., Breckenridge, R. G., Chesley, F. G., Tisza, Laszlo, *Ind. Eng. Chem.* **38**, 1097–109 (1946).
(13) Wells, A. F., "Structural Inorganic Chemistry," p. 463, Oxford University Press, London, 1949.

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Analytical Applications of a Differential Thermal Analysis Apparatus

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▶ **An apparatus for differential thermal analysis is described, which is useful as a tool in the study of inorganic materials. In it have been incorporated as many advantages as possible of systems previously set up. Thermograms of magnesium carbonates and talcs indicate transition and decomposition temperatures. A phase diagram of the potassium niobate–potassium tantalate system was determined from differential thermal analysis data. Thermograms of potassium maleate were prepared from different starting materials. Identification of the magnesium carbonates and talcs according to the source aids in setting up firing schedules in the production of ceramics. The phase diagram of the potassium niobate–potassium tantalate system is of interest in the study of ceramics.**

DIFFERENTIAL thermal analysis has been used for many years for detecting phase transitions, principally in minerals. Excellent reviews of differential thermal analysis apparatus and techniques have been prepared by Grim (*6*) and by Smothers, Chiang, and Wilson (*12*).

In addition to its normal use in determining temperatures of phase transformations, differential thermal analysis is useful as a control tool or as a routine tool for comparing similar but not identical materials. As a control tool it may be used to distinguish raw materials quickly and easily in those cases in which the treatment of the material must be modified if slight changes in the material are encountered. As a comparison tool, differential thermal analysis may be used in some cases to test materials that yield anomalous results by other tests. Determination of transition temperature of samples with systematically varied compositions yields the data necessary to establish the phase diagram of the system.

DESIGN OF APPARATUS

The apparatus used in this work is unique only in that an attempt has been made to incorporate as many advantages as possible of systems previously set up.

The high temperature furnace (Figure 1) was adapted from the design used by Coffeen (*4*).

It has a platinum heating element wound on refractory alumina tubing. A thin cylindrical platinum shield is placed inside the furnace tube. The shield is grounded, with a platinum wire at some convenient point, in order to eliminate noise of thermionic origin. The furnace is mounted on ball-bearing slides and is moved horizontally to enclose or expose the sample holder. To prepare the furnace for use, a platinum–platinum–10% rhodium thermocouple in a $^3/_{32}$-inch insulating tube is placed in the control thermocouple well and the wires are led to the vertical hole in the core and through the ceramic tube to outside terminals. A differential thermocouple consisting of platinum–10% rhodium with a joining wire of platinum, palladium–20% gold, or palladium–10% gold is inserted from the side into two of the sample wells and the wires are led to outside terminals through the four-hole tube. The sample is placed in one of the wells and aluminum oxide as reference material is placed in the other. The furnace is then rolled into place and is ready for use. The furnace thermocouple wires are 0.015 inch and the differential thermocouple wires are 0.005 inch in diameter.

A block diagram of the system built by Leeds & Northrup for controlling the temperature and recording the furnace temperature and differential temperature is shown in Figure 2.

The strip chart recorder is an X_1, X_2 Speedomax Model 69955, which gives a continuous plot of the furnace temperature from the control thermocouple and the differential temperature from the differential thermocouple on a single chart.

The program controller consists essentially of a motor-driven slide-wire so designed that full travel takes place in 2.5 hours. A similar slide-wire is mounted on the shaft of the furnace temperature potentiometer. The signals from the two slide-wires are compared by the control unit, L. & N. Model 10864. The control unit introduces proportional band, reset, and rate time action to control sensitivity and eliminate overshoot and "hunting." The unbalance signal controls a motor-driven Powerstat, located behind the panel, advancing it or backing it off as required to maintain a heating or cooling rate of 10° C. per minute. The stabilized direct current voltage amplifier, L. & N. Model 9835-B, amplifies the differential temperature signal before it is sent to the recorder. It provides six ranges from 25-0-25 μv. to 1-0-1 mv., corresponding for the platinum–10% rhodium *vs.* palladium–20% gold thermocouple to ranges of about 0.7°-0°-0.7° to 27°-0°-27° C.

The equipment is designed to heat the furnace to a preselected temperature from 0° to 1500° C. at a constant rate of 10° C. per minute. When the desired temperature is reached by the furnace, the program unit operates to maintain that temperature or to cool the furnace

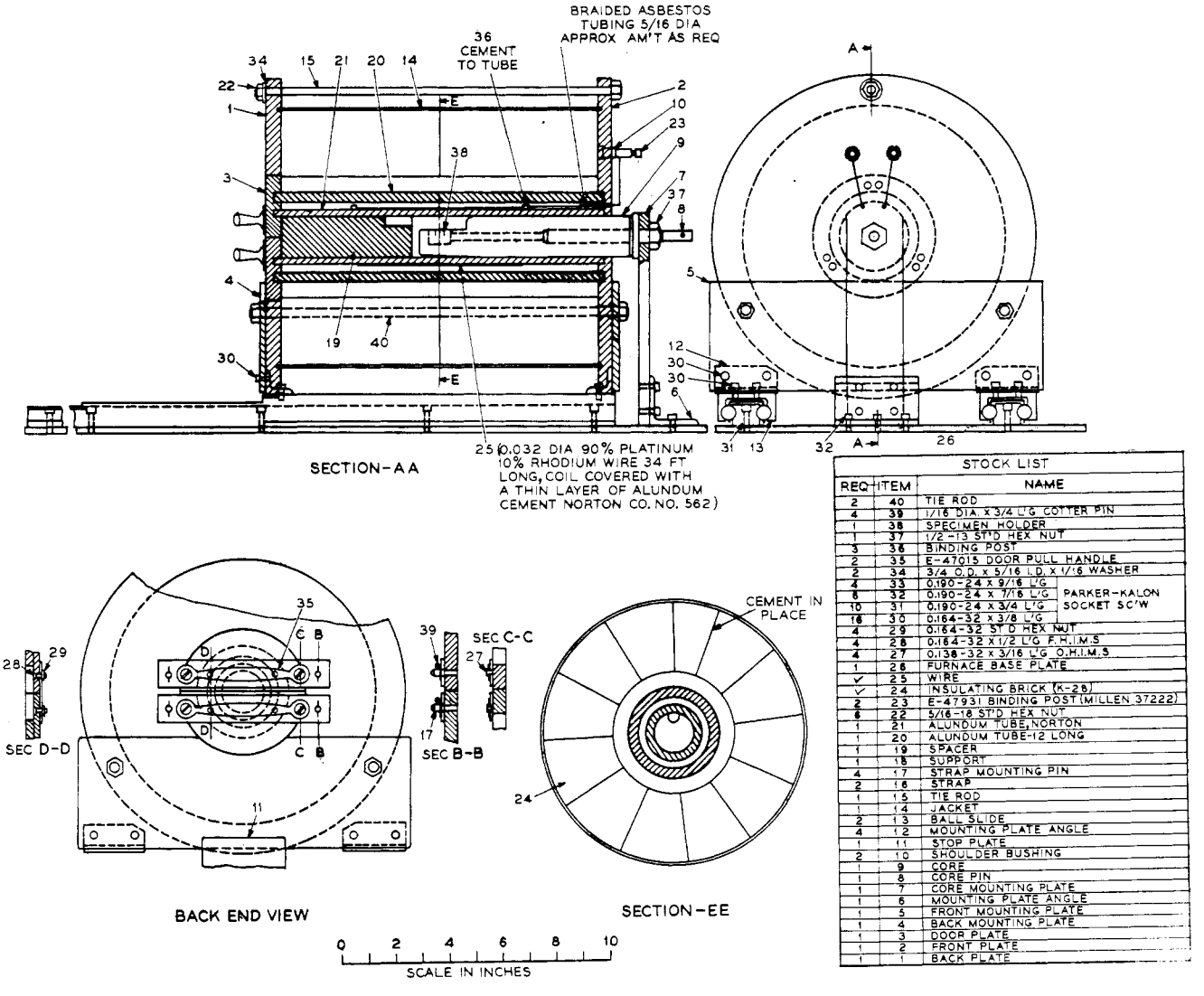

Figure 1. Furnace for differential thermal analysis

Detail No.	Detail	Material	Suppliers
1	Back plate	Transite	Johns-Manville Co
2	Front plate	Transite	Johns-Manville Co.
3	Door plate	Transite	Johns-Manville Co.
4–5	Mounting plate	Steel	
6	Mounting plate angle	Aluminum	
7	Core mounting plate	Aluminum	
8	Core pin	Steel	
9	Core	Refractory alumina	
13	Ball slide	Refractory alumina	Grant Pulley & Hardware Co., Flushing, N. Y.
20	Refractory tube $2^1/_2$-inch I.D.	Alundum	Norton Co.
	Refractory tube $^3/_8$-inch wall	Alundum	Norton Co.
21	Refractory tube $1^1/_2$-inch I.D.	Alundum	Norton Co.
	Refractory tube $^1/_4$-inch wall	Alundum	Norton Co.
24	Insulating brick	K-28	Babcock & Wilcox

at the same rate, depending on the position of a selector switch.

In addition to the functions described, the equipment may be modified easily to give a heating or cooling rate of 0.5° C. per minute. This, with the use of all four holes in the sample holder, will permit the accurate determination of the temperature of a transition by a simple procedure suggested by Keith and Tuttle (*9*).

MATERIALS AND APPARATUS

The magnesium carbonates were: lots 2 and 3, Merck heavy grade, Maryland and California, respectively, and lot 6, Baker heavy grade.

The Montana talc was No. 486 Montana talc, supplied by Whittaker, Clark, and Daniels, Inc. The Sierramic and Yellowstone talcs were California and Montana talcs, respectively, supplied by the Sierra Talc Co.

The potassium niobate and potassium tantalate were prepared from Merck C.P. potassium carbonate, Amend C.P. (99+%) niobium pentoxide, and Amend C.P. (99+%) tantalum pentoxide.

The sample holder, shown in Figure 3, is a platinum cylinder with four wells, the centers of which are equally spaced about the center of the block at a

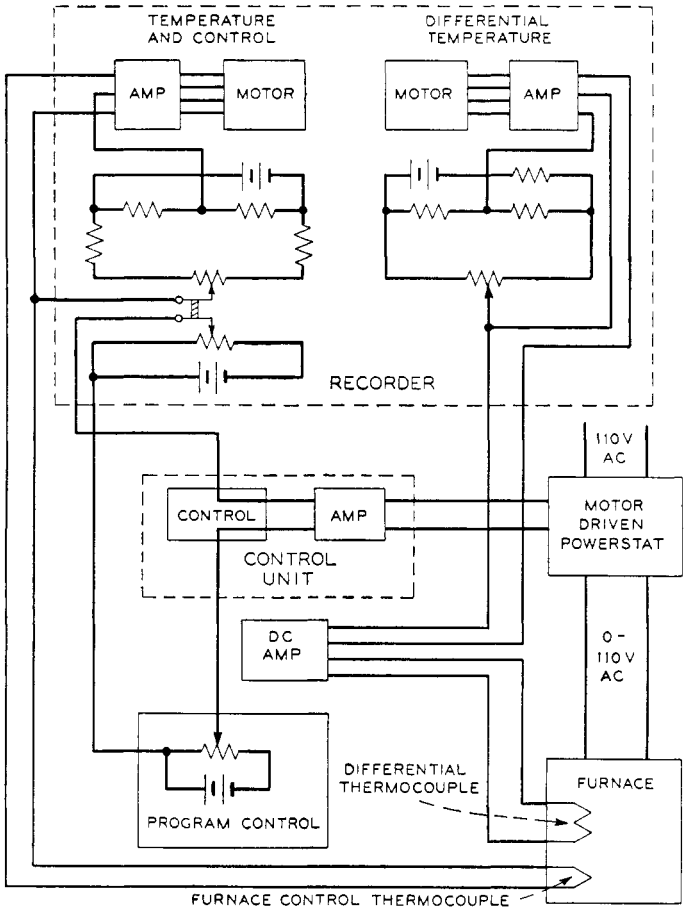

Figure 2. Block diagram of differential thermal analysis equipment

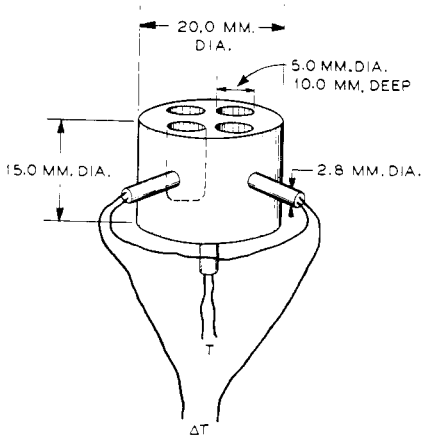

Figure 3. Sample block showing method of introducing thermocouples for furnace temperature, T, and differential temperature, ΔT

radius of 5 mm. The sample holder weighs 82 grams. For most applications only two holes are used. A $^{7}/_{64}$-inch hole is drilled through the side of the block into each well at a depth of 5 mm. to accommodate a thermocouple. A well is drilled from the center of the base of the cylinder to accommodate a control thermocouple.

The platinum cups used in some work are nominally 10 mm. high by 6 to 8 mm. wide. The wall thickness is 15 mils and the weight is 1.8 grams.

EVALUATION OF EQUIPMENT AND METHODS

The first results obtained with the differential thermal analysis apparatus

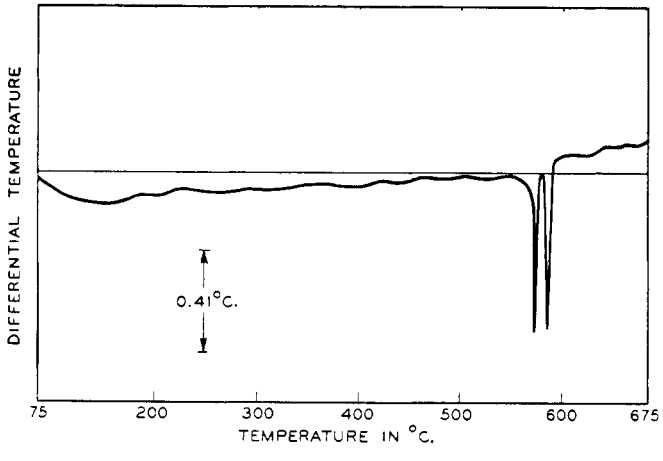

Figure 4. Differential thermogram of mixture of quartz and potassium sulfate

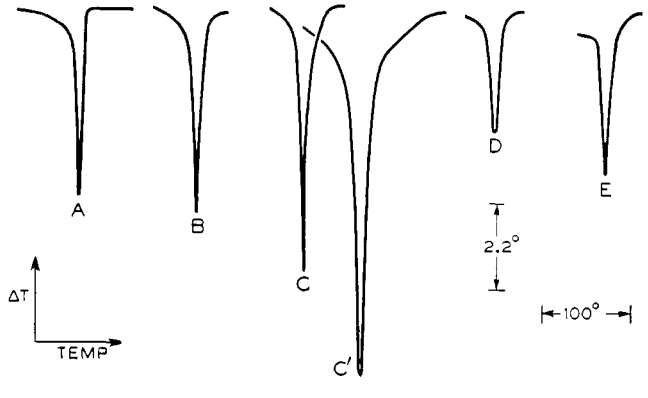

Figure 5. Comparison of sample holders for potassium sulfate transition (170-mg. sample)

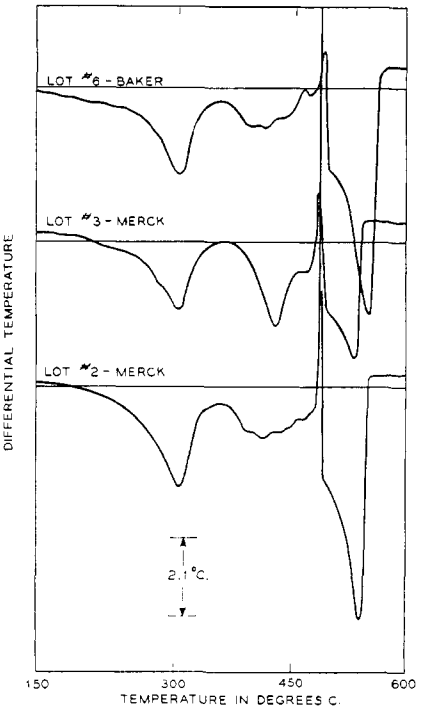

Figure 6. Differential thermograms of commercial magnesium carbonates

were thermograms of known transitions, which were used in order to become familiar with the range and sensitivity of the apparatus. A typical thermogram is shown in Figure 4. The sample consisted of a mixture of quartz and potassium sulfate. The reference material was aluminum oxide. The scale on the differential temperature is 100-0-100 μv. The deflections are due to α-β transitions in quartz (SiO_2) and potassium sulfate, respectively. The thermogram shows the temperatures of transition at 571° and 580° C., in good agreement with Silverman and associates (*11*), who give the transition points at 573° and 583° C., respectively. The transition temperatures were determined by the intersection method (*9*). The magnitude of the deflection corresponds to a differential temperature of approximately 0.7° C. The differential thermocouple was made from 90% platinum–10% rhodium and 60% palladium–40% gold. The higher gold content of the alloy provides an increase in sensitivity at some sacrifice in useful temperature range.

Another method of handling of the sample uses a core- and wire-supported pair of metal cups with the sample and reference materials. Some investigators (*8*) claim that this method permits greater sensitivity because there is no large heat reservoir in contact with the sample. Other investigators (*7*) have used ceramic blocks, claiming the same increased sensitivity because of the low heat conductivity of the block material.

Figure 5 shows thermograms of the potassium sulfate transition at 583° C. with a variety of sample holders.

Thermogram *A* was obtained using the platinum block (82 grams) previously described. The sample weight was 170 mg. *B* was obtained by using platinum cups (15-mil wall, 1.8 grams) supported in an insulating firebrick core. The sample consisted of 170 mg. of potassium sulfate mixed with enough aluminum oxide to fill the cup. *C* was obtained in a similar manner, except that the cups were set into loops of platinum wire. *C'* was obtained by the same method, but with the cup filled with potassium sulfate. *D* was obtained using 170 mg. of potassium sulfate and a small amount of aluminum oxide in fused quartz cups set in wire loops. The final thermogram, *E*, was obtained with the same sample as in *B* and *C*, but the cups were fabricated from 1.5-mil platinum sheet.

The ratios of total height to half widths of the deflections are about 25,

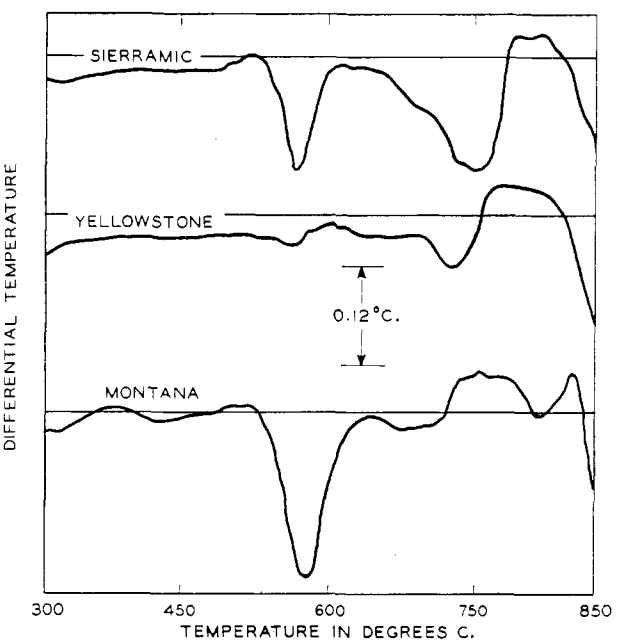

Figure 7. Differential thermograms of Montana, Yellowstone, and Sierramic talcs using platinum cups

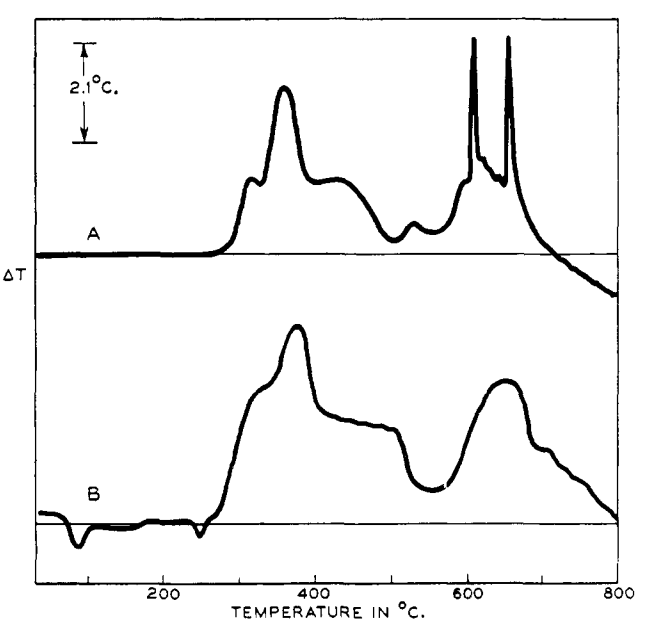

Figure 8. Thermograms of potassium maleate

A. Maleic anhydride
B. Diethyl maleate

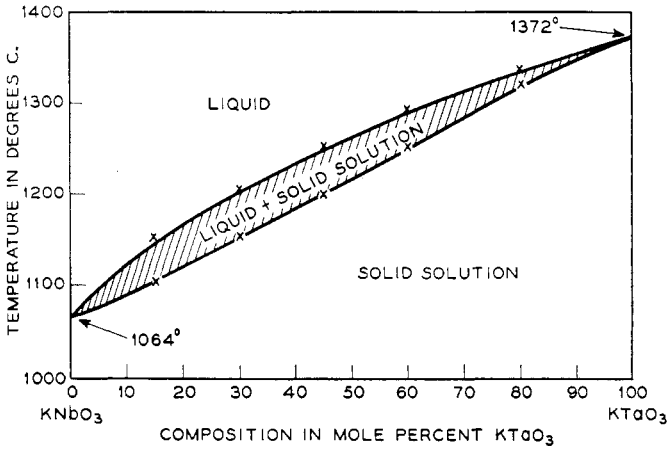

Figure 9. Phase equilibrium relationships at the solidus for system $KNbO_3$–$KTaO_3$

23, 39, 11, and 14, for *A*, *B*, *C*, *D*, and *E*, respectively. The comparatively wide deflections in *D* and *E* indicate that the sample holder is not at a uniform temperature. This effect is probably due to poor heat transfer around the cup because of the poor thermal conductivity of quartz in one case and the very thin cross section of the platinum in the other case. The resulting nonhomogeneity of temperature could permit a portion of the sample to begin its phase transformation well ahead of portions in contact with other parts of the cup. The effect on the difference signal would be a lowering and broadening of the peak.

The conclusion obtainable from these curves is that the use of cups does permit a gain in sensitivity. The cup walls should be thick enough to provide for thermal equilibrium about the cup. There was no indication of error in the measurement of the transition temperature.

EXPERIMENTAL RESULTS

A series of differential thermograms of magnesium carbonate and talc was obtained in order to determine whether or not the method showed promise as an aid in quality control of steatite ceramics. The platinum block was used as the sample holder. The method shows distinct differences in the thermal history of both the magnesium carbonate and the talc. Beck (*3*) shows thermograms for nesquehonite and lansfordite which are similar in gross structure to the thermograms of magnesium carbonates in Figure 6.

Thermograms of three samples of talc are shown in Figure 7. In each case a strong endothermic reaction begins at about 850° C. The magnitude of the reaction is about the same in each case, but differences due to impurities make it possible to distinguish one from the other. The Montana and Sierramic talcs show a small broad endothermic reaction in the neighborhood of 570° C. The Sierramic talc also shows a fairly large endothermic effect in the neighborhood of 700° C. This reaction occurs to a lesser extent in the Yellowstone talc, but not in acid-washed samples of either talc.

In order to permit a precise interpretation of the thermograms of Figures 6 and 7, the data obtained would have to be correlated with weight loss and x-ray data. There are, however, sufficient differences in the three thermograms to enable identification of samples having a similar mineralogical composition. The differential thermocouple for the magnesium carbonate and talc studies was of 90% platinum–10% rhodium *vs.* 80% palladium–20% gold.

As part of a study of polyester resins, one observer (*13*) attempted to determine the degree of completeness of precipitation of maleate as potassium maleate. The amount of maleate precipitated was determined gravimetrically (*2*) and polarographically (*5*). An anomaly was observed, in that with certain starting materials the polarographic method showed less than one half the quantity of maleate that was indicated by the gravimetric method, while with other starting materials the results were in agreement. Differential thermograms of representative samples were obtained. The two thermograms shown in Figure 8 indicate that the precipitates obtained with the two starting materials are quite different. Further study of this phenomenon has been started.

Potassium niobate was investigated because of its interest as a ferroelectric. The compound is normally prepared from potassium carbonate and niobium pentoxide. A phase diagram of the potassium carbonate–niobium pentoxide system has been prepared by Reisman and Holtzberg (*10*). The melting point of potassium niobate has been reported over a range of temperatures from 1020° to 1125° C. Preliminary investigation indicates that the variable results are due to nonstoichiometric preparation of the potassium niobate. A carefully prepared stoichiometric system yielded a melting point of 1064° ± 2° C.

In Figure 9, the phase equilibrium relationships as determined by differential thermal analysis are shown for the binary system between the isostructural ferroelectric compounds $KNbO_3$ and $KTaO_3$. As the mixed system showed strong supercooling tendencies (evidenced by large exotherms in solid solution mixtures slightly below the solidus), data determination was limited to the heating cycle only. The solidus temperature is marked by initial endothermic departure of the differential signal from its base line; the cessation of the endothermic effect marks the liquidus temperature. The extrapolation of the mixed system to the $KTaO_3$ end member is shown to coincide closely with the melting point established by independent methods at 1372° C. The data for this phase diagram were obtained using wire-supported platinum cups and a platinum *vs.* platinum–10% rhodium differential thermocouple.

REFERENCES

(1) Ahrens, L. H., *Geochim. et Cosmochim.* **2**, 168–9 (1952).
(2) Am. Soc. Testing Materials, Philadelphia, Pa., "Official and Tentative Methods," ASTM D 563-52.
(3) Beck, C. W., *Am. Mineralogist* **35**, 985–1013 (1950).
(4) Coffeen, W. W., Metal & Thermit Corp., Rahway, N. J., private communication.
(5) Garn, P. D., Halline, E. W., ANAL. CHEM. **27**, 1563–5 (1955).
(6) Grim, R. E., *Ann. N. Y. Acad. Sci.* **53**, 1031–53 (1951).
(7) Grimshaw, R. W., Heaton, E., Roberts, A. L., *Trans. Brit. Geram. Soc.* **44**, 76–92 (1945).
(8) Gruver, R. M., *J. Am. Ceram. Soc.* **31**, 323–8 (1948).
(9) Keith, M. L., Tuttle, O. F., *Am. J. Sci., Bowen Vol.* Pt. 1, 203–80 (1952).
(10) Reisman, A., Holtzberg, F., *J. Am. Chem. Soc.* **77**, 2115–9 (1955).
(11) Silverman, A., Insley, H., Morey, G. W., Rossini, F. D., "Data on Chemicals for Ceramics Use," *Natl. Research Council Bull.* **18**, 94, 102 (1949).
(12) Smothers, W. J., Chiang, Y., Wilson, A., "Bibliography of Differential Thermal Analysis," Univ. Arkansas Inst. Sci. and Technol. Research Ser., No. 21 (November 1951).
(13) Vincent, S. M., Bell Telephone Laboratories, Inc., Murray Hill, N. J., unpublished measurements.

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