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THE CALCINATION IN AIR OF BERYLLIUM OXALATE TRIHYDRATE TO BERYLLIUM OXIDE

R. L. Hamner
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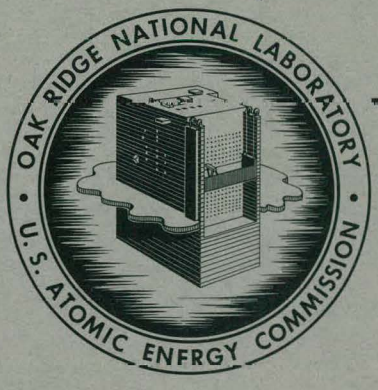

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SUMMARY

Variations in sinterability of high-purity BeO powders obtained by calcining $BeC_2O_4 \cdot 3H_2O$ led to an investigation of the phase changes occurring during the calcination process.

Studies were made under continuous and equilibrium heating conditions, using differential thermal analysis, thermogravimetric measurement, and room- and high-temperature x-ray analysis. Beryllium oxalate trihydrate decomposed to $BeC_2O_4 \cdot H_2O$ when heated in air at 50°C, given sufficient time. A liquid phase was observed during decomposition to $BeC_2O_4 \cdot H_2O$ under rapid heating conditions between 80 and 150°C; this effect was not observed under "equilibrium" heating conditions at 100°C or below.

The monohydrate was observed to decompose between 225 and 250°C. Complete decomposition to BeO was accomplished at 275°C and might occur as low as 250°C. No stable intermediate compounds except $BeC_2O_4 \cdot H_2O$ were indicated during the calcination process.

INTRODUCTION

This study was undertaken as part of a development program directed toward the definition and control of variables affecting the sinterability of high-purity BeO powders obtained by calcining $BeC_2O_4 \cdot 3H_2O$ in air. In preliminary studies, variations in sinterability were observed in BeO powders derived from different batches of the oxalate which could not be explained on the basis of purity, calcining temperature, surface area, or fabrication procedure. A logical first step in investigating this problem was to characterize the starting material with respect to phase changes occurring under varying conditions of time and temperature during calcination in air. The material chosen for study was prepared by the Beryllium Corporation and was identified as single-phase, polycrystalline $BeC_2O_4 \cdot 3H_2O$ by x-ray diffraction analysis and by means of a polarizing microscope.

PROCEDURE AND EXPERIMENTAL METHODS

Calcination Studies During Continuous Heating

Initial studies were carried out under continuous heating to simulate calcining conditions which might be encountered in practice. Samples of $BeC_2O_4 \cdot 3H_2O$, weighing approx 0.75 g, were calcined at a constant, rapid heating rate to BeO in practically stagnant air. An apparatus was used similar to that developed by the National Bureau of Standards[1] which provided for the simultaneous recording of differential thermal analysis (D.T.A.) and weight change. The samples for these determinations were heated in the same furnace in close proximity to each other and to the D.T.A. standard sample of Al_2O_3 and a Pt vs Pt–10% Rh furnace thermocouple embedded in Al_2O_3.

Calcination Under "Equilibrium" Heating Conditions

Studies of the calcination process also were made under "equilibrium" heating conditions to determine the existence of other effects which might not be detectable under continuous, constant-rate heating.

Samples of $BeC_2O_4 \cdot 3H_2O$, weighing approx 30 g, were placed in porcelain crucibles and heated in practically stagnant air to a series of successively high temperatures until "equilibrium" conditions were attained. "Equilibrium" conditions at a given temperature were said to have been reached when the weight change of the sample over a 24-hr period was less than 0.1%.

Initial heating at 50 to 150°C was accomplished in a drying oven, using a thermometer placed near the samples to measure temperature. At 175°C and above, heating was accomplished in a muffle furnace, with a Chromel-Alumel thermocouple placed near the samples. Weight change was determined by removing samples periodically and weighing as soon as they had cooled to room temperature. Phases present at "equilibrium" were determined by x-ray analysis and by means of a polarizing microscope.

X-Ray Methods

A high-angle x-ray diffractometer using Cu Kα (λ = 1.5418) radiation was employed in the examination of all samples. High-temperature x-ray examinations were made using a furnace attachment to the x-ray apparatus.

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[1] Nat. Bur. Standards (U.S.), Tech. News Bull, 37(6), 1953.

Temperatures were determined by a Chromel-Alumel thermocouple placed in contact with the sample, and x-ray patterns were recorded during heating of $BeC_2O_4 \cdot 3H_2O$ until dissociation to BeO was complete.

PRESENTATION AND DISCUSSION OF RESULTS

Figure 1 shows the D.T.A. curve indicating the phase changes occurring during calcination at the rate of 7°C/min.

An endothermic reaction is indicated, beginning at approx 80°C, which proceeded rapidly to a thermal arrest at approx 130°C and then continued to approx 150°C. During this reaction the sample became liquid and then solidified into a hard mass which was extremely difficult to remove from the sample containers. Larger samples of $BeC_2O_4 \cdot 3H_2O$, weighing approx 30 g, when heated at the same rate, were observed to expand upon solidification with sufficient force to break a fused silica or alumina container. The temperatures of liquefaction and solidification were not determined, but the liquid state was noted in the region of the "arrest" on the D.T.A. curve designated as quench point 1. At this point the weight loss corresponded very closely to the theoretical for $BeC_2O_4 \cdot 2H_2O$ (approx 12%); however, no evidence of a distinct phase corresponding to this composition was found by room-temperature or high-temperature x-ray analysis. The quench sample at this point contained two phases: $BeC_2O_4 \cdot 3H_2O$ and $BeC_2O_4 \cdot H_2O$. An x-ray pattern for the monohydrate was not reported in the literature; its designation is based on chemical analysis and weight change from decomposition of the trihydrate. The x-ray data for this compound is listed in Table 1.

Single-phase material was obtained at quench point 2 (approx 150°C), where the reaction was practically complete, and at quench point 3 (approx 250°C) according to microscopic examination. X-ray analyses supported by weight loss from the trihydrate showed this material to be $BeC_2O_4 \cdot H_2O$. According to these data, then, the first reaction proceeded directly to the monohydrate through the simultaneous loss of two loosely held molecules of H_2O.

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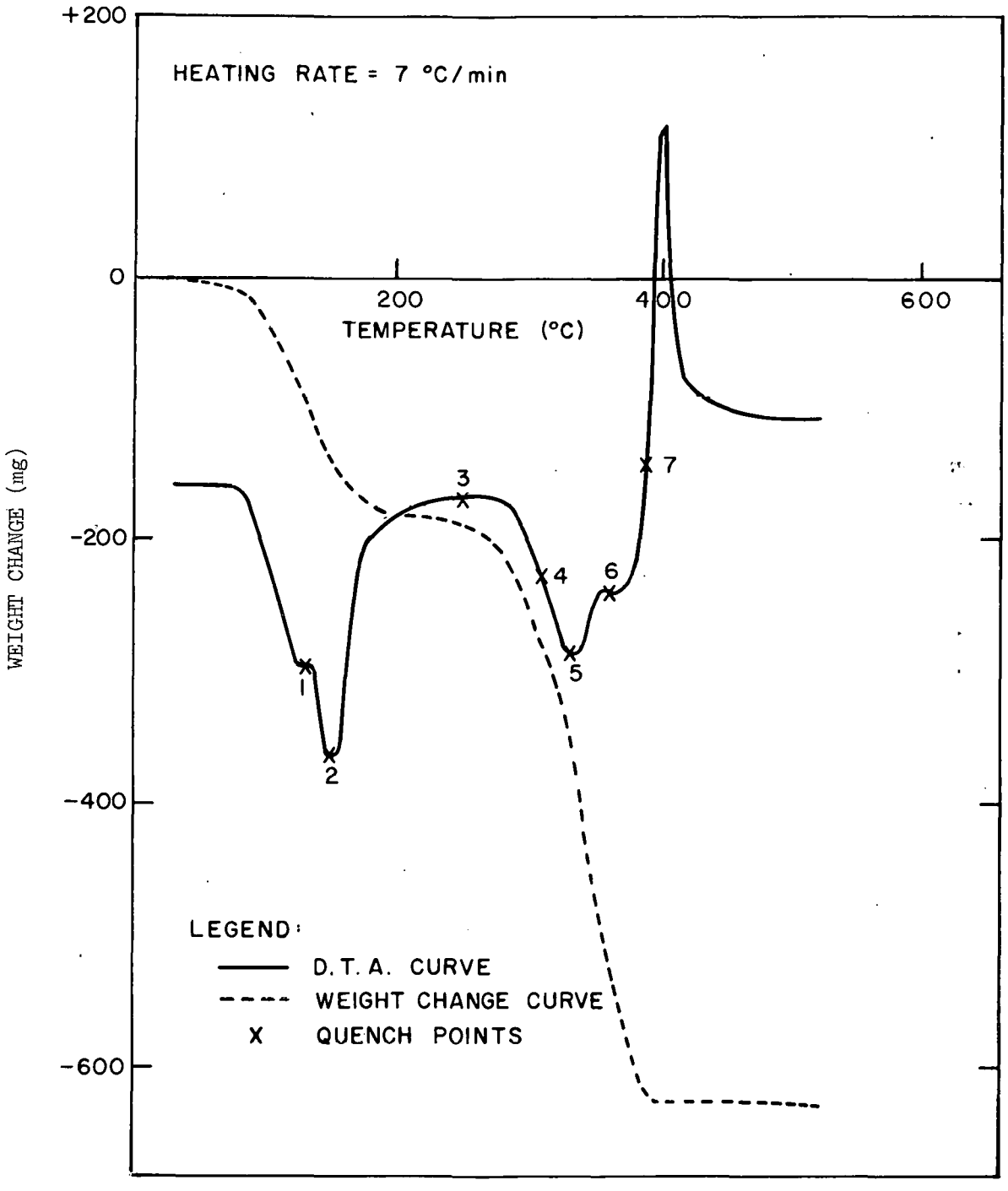

Fig. 1 Differential Thermal Analysis and Weight-Change Curves During Calcination of $BeC_2O_4 \cdot 3H_2O$ to BeO.

Table 1. Powder Diffraction Data for $BeC_2O_4 \cdot H_2O$

I	d (A)
S	7.03
M	6.02
VS	3.97
M	3.82
W	3.55
M	3.43
S	3.07
VW	3.02
VW	2.96
W	2.87
W	2.65
S	2.47
W	2.44
W	2.40
W	2.37
MW	2.28
W	2.26
W	2.21
VW	2.045
VW	1.99

The D.T.A. curve indicated a second endothermic reaction between approx 260 and 340°C. X-ray analysis of samples air-quenched during this reaction (quench points 4 and 5) showed the presence of $BeC_2O_4 \cdot H_2O$ only. Since the D.T.A. and weight-change curves showed that a reaction was in progress, it was assumed that some reaction products were present that were not detected by x-ray analysis either because of quantity or because of a noncrystalline nature. Chemical analysis of samples decomposed to the same weight loss (approx 54%) as that obtained for the thermogravimetric sample at quench point 5 showed the oxalate radical (C_2O_4) and H_2O to be present in a 1:1 molar ratio, as in the monohydrate. According to weight loss and chemical analysis, one-half of the monohydrate had been decomposed at this point. It was observed that small quantities of CO and CO_2 in the molar ratio of 2.3:1 were present as part of the decomposition products, although the significance of this observation is not understood.

The presence of BeO was first noted at approx 370°C (quench point 6). Line broadening in the x-ray diffraction pattern indicated that this product was apparently in a very finely divided state. The weight-change curve, which showed a continuing weight loss at this point, indicated that complete decomposition to BeO had not occurred.

Complete decomposition to BeO was apparently accomplished at approx 390°C, where D.T.A. revealed a sharp exotherm, marking the end of the calcination process as evidenced by weight change and a very sharp x-ray diffraction pattern for BeO.

In discussing the phase changes which occur during the calcination of $BeC_2O_4 \cdot 3H_2O$ to BeO during continuous heating, it must be noted that temperature relationships are as determined by specific conditions of heating rather than by an exact determination of sample temperature; this is demonstrated by Fig. 2, which shows thermograms of the calcination process during continuous heating at different heating rates: 3 and 7°C/min.

Figure 3 shows a thermogram of $BeC_2O_4 \cdot 3H_2O$ samples heated under "equilibrium" conditions. It is apparent that the trihydrate is thermally unstable in air and may decompose at temperatures as low as 50°C, given

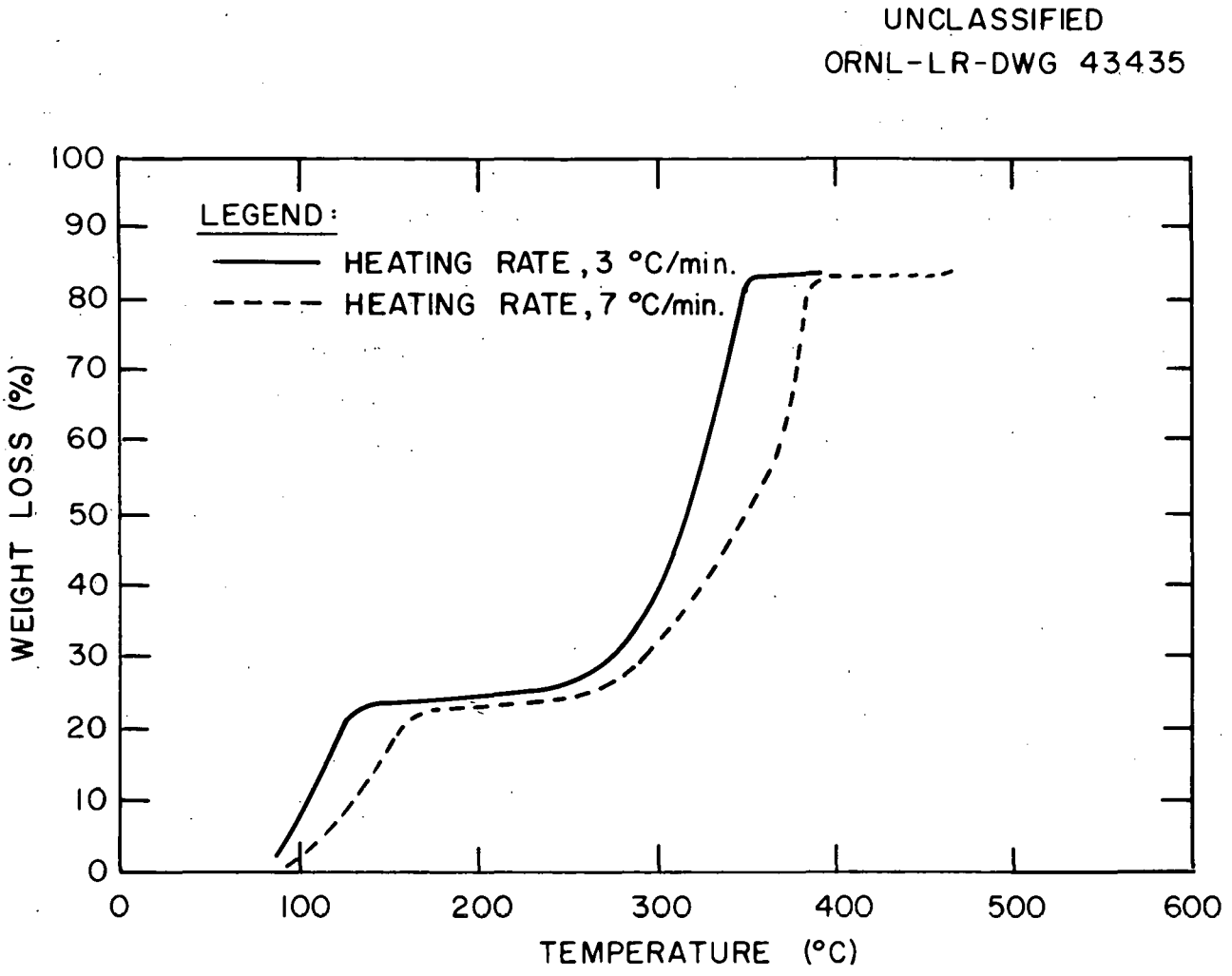

Fig. 2 Continuous Heating Thermograms for Calcination of $BeC_2O_4 \cdot 3H_2O$ to BeO.

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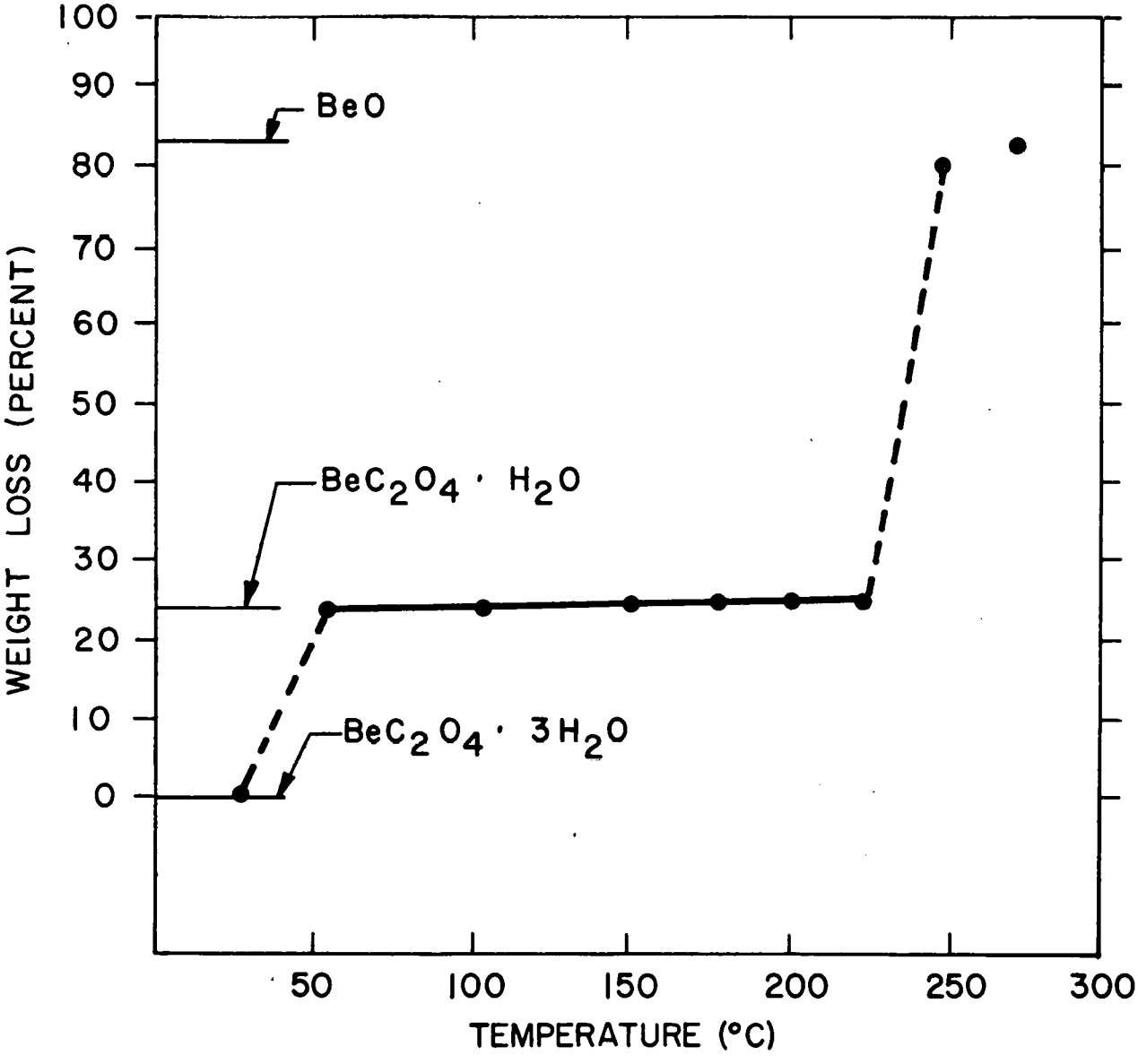

Fig. 3 "Equilibrium" Thermogram for Calcination of $BeC_2O_4 \cdot 3H_2O$ to BeO.

sufficient time. The decomposition behavior of the trihydrate under these conditions was observed to differ significantly from that under continuous heating. When decomposition was allowed to proceed slowly under "equilibrium" heating conditions at 100°C or below, a liquid phase was not observed, and a shrinkage rather than an expansion of the product occurred. Weight change, x-ray analysis, and microscopic examination indicate that $BeC_2O_4 \cdot H_2O$ is the only phase present between 50 and 225°C. When heated at 250°C, the monohydrate decomposed. In this plot, the weight-loss point shown at 250°C simply represents the weight loss observed on the date of plotting.

Figure 4 shows the time vs weight-loss dissociation characteristics of the monohydrate heated at constant temperatures of 250, 275, and 320°C. The dotted line extension of the 250°C curve denotes a continuing weight loss beyond the time shown. It is very evident that there are distinct changes in dissociation rate with time, dissociation being rapid initially and very slow as it approaches completion. Studies were not conducted to determine the cause of the change in dissociation rate with time, although it is felt that insulation by the products of decomposition and the partial pressure of CO_2 and H_2O in the surrounding atmosphere may be contributing factors.

Figure 5 shows high-temperature x-ray diffraction patterns obtained on heating $BeC_2O_4 \cdot 3H_2O$ at successively higher temperatures and is generally descriptive of the calcination process with respect to phase changes occurring during decomposition. Pattern (B) represents the first decomposition step, where a two-phase region composed of the trihydrate and the monohydrate exists until decomposition to the monohydrate is complete. Patterns (C), (D), and (E) are indicative of the thermal stability of the monohydrate. The final decomposition step is represented in pattern (F), where BeO first appears, with considerable line broadening, as the monohydrate is decomposing. Pattern (G) marks the end of the calcination with complete decomposition to BeO. Further calcination in air at higher temperatures results only in an increase in particle size of the BeO powder.

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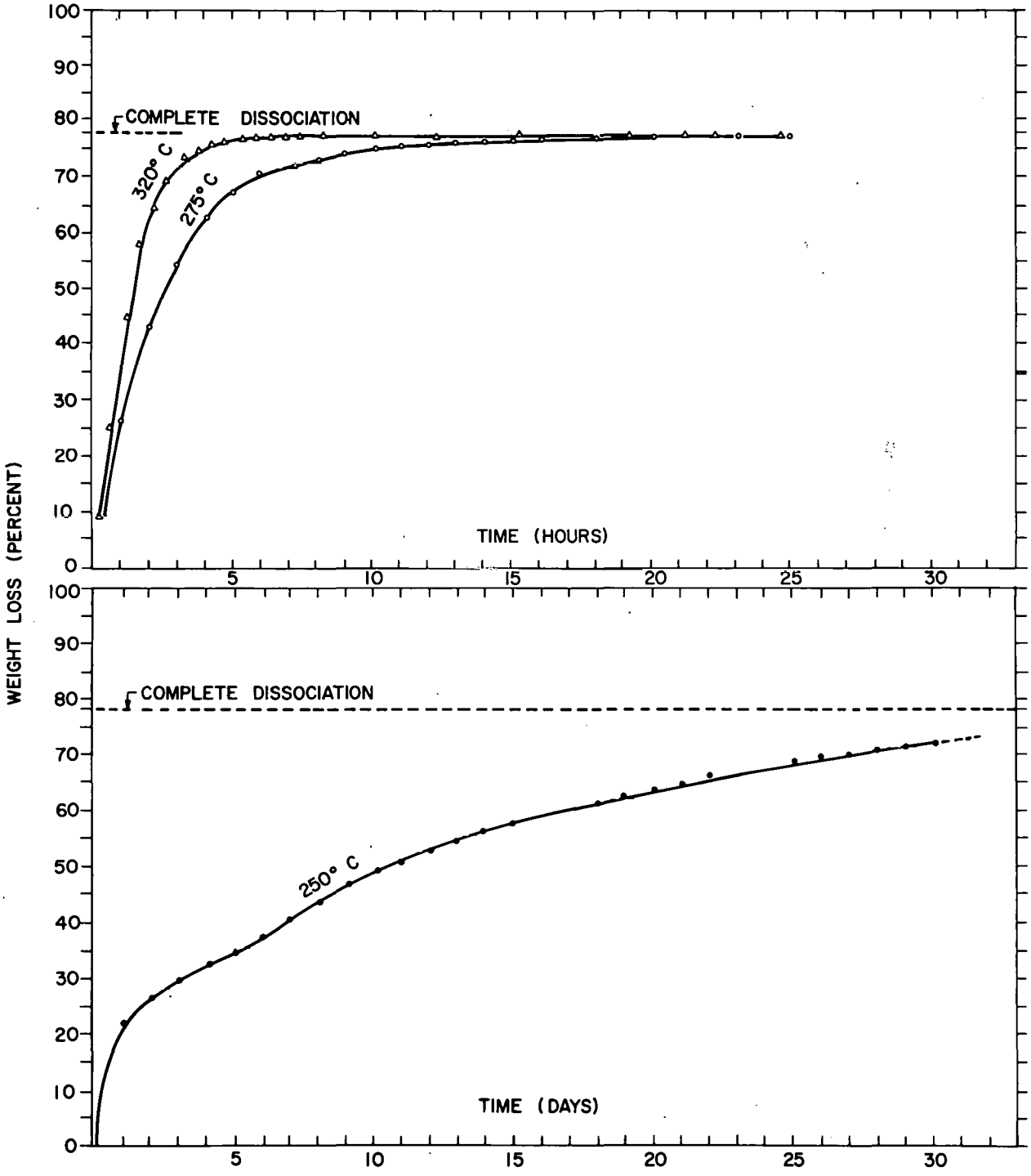

Fig. 4 Time vs Weight-Loss Curves for Dissociation of $BeC_2O_4 \cdot H_2O$ to BeO.

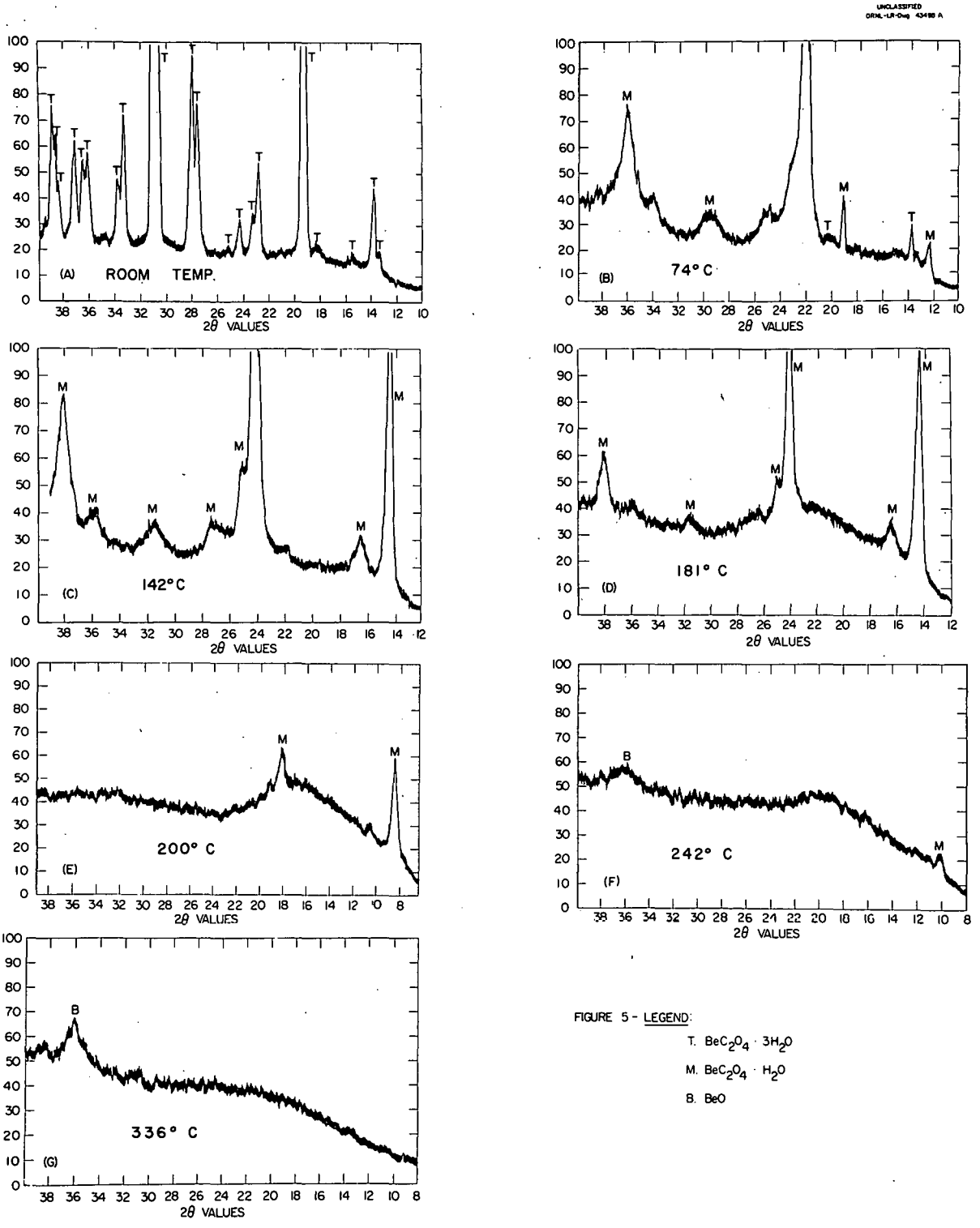

Fig. 5 High-Temperature X-Ray Patterns Obtained During Calcination of $BeC_2O_4 \cdot 3H_2O$ to BeO.

CONCLUSIONS

1. $BeC_2O_4 \cdot 3H_2O$ is relatively unstable in air at low temperatures and may be decomposed to $BeC_2O_4 \cdot H_2O$ as low as 50°C.

2. The first step in the decomposition of $BeC_2O_4 \cdot 3H_2O$ is the simultaneous loss of two molecules of water of hydration.

3. The physical dissociation characteristics of $BeC_2O_4 \cdot 3H_2O$ to $BeC_2O_4 \cdot H_2O$ are dependent upon heating rate.

4. A liquid phase is formed during rapid decomposition of $BeC_2O_4 \cdot 3H_2O$ to $BeC_2O_4 \cdot H_2O$ which expands forcefully upon solidification.

5. $BeC_2O_4 \cdot H_2O$ is relatively stable in air compared with $BeC_2O_4 \cdot 3H_2O$, but begins to decompose above 225°C.

6. $BeC_2O_4 \cdot H_2O$ is the only stable intermediate compound formed during decomposition of $BeC_2O_4 \cdot 3H_2O$ to BeO.

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