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DIFFERENTIAL THERMAL ANALYSIS OF PHASE EQUILIBRIA IN MIXTURES OF ANHYDROUS CARBONATES.
III. K_2CO_3–$BaCO_3$

ROGER E. MILLS * and R. THOMAS COYLE **

Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401 (U.S.A.)

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ABSTRACT

The mixtures $(K_2CO_3)_{1-x}$–$(BaCO_3)_x$ were studied in a Perkin–Elmer DTA 1700 instrument operated in the DSC mode. A solid solution was found to exist for $x < 25$ mol%. A eutectic line at 783 ± 1 ° C extended from 25 to 80 mol% with $x_{eu} = 44.0$ mol%, terminating at a compound $K_2Ba_4(CO_3)_5$. That compound was observed to melt incongruently at 899 ± 3 ° C, for x in the interval (55,100) mol%. Polymorphic transformations occur at 808 ± 1 ° C for $x > 80$ mol%, and at 970 ± 1 ° C for $x > 60$ mol%. For low x, the melting temperature increases from 903 ± 1 ° C for pure K_2CO_3 to 917 ± 1 ° C at $x = 6$ mol% before beginning the normal decrease in liquidus for increasing x.

INTRODUCTION

Investigation of mixtures of carbonates of interest as potential thermal storage media in central solar receivers [1] has been continued with studies of mixtures of K_2CO_3 and $BaCO_3$. The thermal data for $BaCO_3$ compiled by Stern and Weise [2] are reviewed in ref. 1. The melting temperature for pure K_2CO_3 is given [2] as 898 ± 2 ° C, where a latent heat of 27 kJ mol^{-1} is required. Very little earlier information on these mixtures is available in the literature. Le Chatelier reported [3] study of a quaternary system involving these salts together with Na_2CO_3 and $CaCO_3$, but no information specific to the binary mixture of present interest appears. He did report observation of a double salt $K_2Ba(CO_3)_2$ melting at 800 ° C on a scale on which the melting point of Au was 1045 ° C. No contradictions of that observation have previously been reported.

In the present work, observations of phase transitions have been made in mixtures with x_{BaCO_3} in the range 2–96 mol% using Perkin–Elmer DTA

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* Permanent address: Department of Physics, University of Louisville, Louisville, KY 40292, U.S.A.

** Present address: UNOCAL Science & Technology Division, UNOCAL Corporation, 376 S. Valencia, Brea, CA 92621, U.S.A.

1700 equipment operated in a mode giving calculated DSC data. These data have been interpreted in part by using a version of Tammann's Rule [1,4].

EXPERIMENTAL

Materials

Anhydrous barium carbonate and potassium carbonate reagents of the Gold Label standard (99.999%) series were obtained from the Aldrich Chemical Company. The reagents were stored in a dry box and were tested periodically for hydration by observation of heating of the pure reagents. Whereas the $BaCO_3$ showed stable masses and little or no signs of peaks below 400 °C which might be indicative of dehydration, the K_2CO_3 was extremely acquisitive of H_2O. X-ray diffraction studies [5,6] and infrared absorption measurements [7] showed the presence of only those materials expected as a result of reaction of a portion of the anhydrous K_2CO_3 with traces of water. On first heating, from 200 to 250 °C the samples showed peaks interpreted as a reversal of the absorption reaction. It was found that these peaks did not reappear after initial heating, and that sample masses were stable after the initial H_2O losses occurred, to within ± 0.2 mg for sample masses of about 25 mg.

Procedure

All measurements were made by heating runs, at $+10\,°C\ min^{-1}$, in a Perkin–Elmer DTA 1700 apparatus operated in the DSC mode. All runs were conducted using a purge gas of dry CO_2 at a flow rate of 40 ml min^{-1}. No signs of high-temperature decomposition were observed. Sample masses and platinum crucible masses were stable in runs up to 1000 °C. No discoloration of the crucibles was observed indicating that no significant carbonate ion decomposition occurred. All masses were determined to 0.01 mg using a Mettler H51AR balance. Sample compositions were determined using masses determined after any bicarbonate had been decomposed by heating. Separate observations that such decomposition did not involve the $BaCO_3$ component allowed inference of the mass of the K_2CO_3 remnant in the sample. Samples were usually mixed by grinding, and further homogenized by heating to about 950 °C, to permit diffusion. For samples of very low minority composition, the minority component was added directly to a sample with a known quantity of the majority component.

Homogeneous compositions, as evidenced by the sharpness and shape of transition peaks, were readily obtained at low $BaCO_3$ concentrations. No alterations of thermal characteristics were observed after initial melts, regardless of any differences in exposure to high temperature. At high $BaCO_3$

concentrations, the occurrence of incongruent melting did lead to inhomogeneous concentrations in the samples unless the sample was subjected to extended heat at a temperature just below the temperature (899 ± 3° C) at which the incongruent melting was observed. The strength of spurious transitions (the $\gamma \rightarrow \beta$ polymorphic transition for $x_{BaCO_3} < 80$ mol% or the eutectic transition for $x_{BaCO_3} > 80$ mol%) indicative of remnant inhomogeneity decreased with increasing time of heat treatment. For x_{BaCO_3} near 80 mol%, the maximum time needed to eliminate the spurious peaks was about 2 h. (Further additional heating for up to 14 h was tried, without visible effect.) Less time was needed for concentrations further removed from 80 mol%. This procedure could not assure that some small regions of non-uniform concentration did not occur. In the very small samples (< 25 mg) it did not seem likely that segregation would occur, but an inspection of sections was not feasible in this configuration.

RESULTS

Examples of the DSC traces are shown in Figs 1 and 2. The peak temperatures are noted for comparison in these figures. It can be seen in Figs. 1(a)–(e) that a region of solid solution exists for low $BaCO_3$ concentrations, up to at least 23.1 mol%. The single peak remains narrow, indicating nearly isothermal melting for $BaCO_3$ concentrations up to about 10 mol%. At that point, the leading edge of the melting peak begins to round and to commence at lower temperatures. It is interesting that the onset of the melting occurs in this range at higher temperatures than that required for melting of pue K_2CO_3. This is also apparent from the data for the melting peaks given in Table 1. The corresponding portion of the phase diagram, Fig. 3, is shown as a single line because the narrowness of the melting peaks in this region do not permit differentiation of solidus and liquidus temperatures. The increase in the melting temperatures is well outside the resolution capability of the equipment at these temperatures. The samples, when slowly cooled, showed a residual localized yellowish coloring at the concentrations near those (6 mol%) of highest melting temperature. Both the pure reagents and mixtures at other concentrations were uniformly white.

The onset and progressive change of the eutectic feature is shown in Figs. 1(f)–(k). The location of the peak in the continuous melt feature, interpreted as the liquidus, is much more clearly defined for $BaCO_3$ concentrations below 45 mol% than above that value. The disappearance of the liquidus is complete in Fig. 1(l), when the peritectic melting has appeared. At these higher values of x_{BaCO_3}, the changes in heat capacity near and at the liquidus are too small to be distinguishable from the normal curvature of the baseline.

Incongruent or peritectic melting is sometimes encountered in alloys or salt mixtures in which it is possible to heat the sample sufficiently to reach a

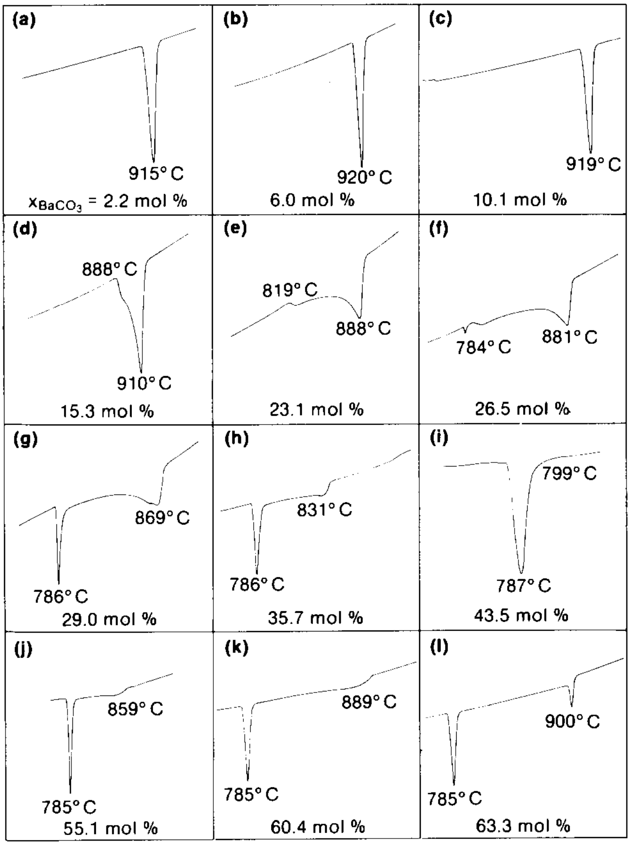

Fig. 1. DSC traces typical of K_2CO_3–$BaCO_3$ mixtures, x_{BaCO_3} less than 64 mol%. Not all vertical scales are the same.

liquid phase of homogeneous composition. A homogeneous solid sample is then obtained by quench cooling so that resegregation does not have time to occur. Since $BaCO_3$ decomposes prior to melting under the pressures at which these experiments were conducted, this procedure could not be employed. Instead, a procedure of heat treatment was used to obtain nearly homogeneous samples.

The portions of Fig. 2 compare the traces recorded with rapid cooling (Figs. 2(a), (c), (g)) subsequent to peritectic melting with the traces observed in samples of similar composition (Figs. 2(b), (d), (h)) in which the sample was heat treated to promote recombination of the ions separated in the incongruent melting. It can be seen that with proper heat treatment, only the eutectic melt is observed, and no $\gamma \rightarrow \beta$ transition, for $BaCO_3$ concentrations below 80 mol%. For $BaCO_3$ concentrations above 80 mol% only the $\gamma \rightarrow \beta$ transition, and no eutectic, is seen in Fig. 2(h), both before and after the peritectic melting. Figures 2(e) and (f) show the effect of heat treatment on a single sample with $BaCO_3$ concentration of 80.5 mol%. (The vertical

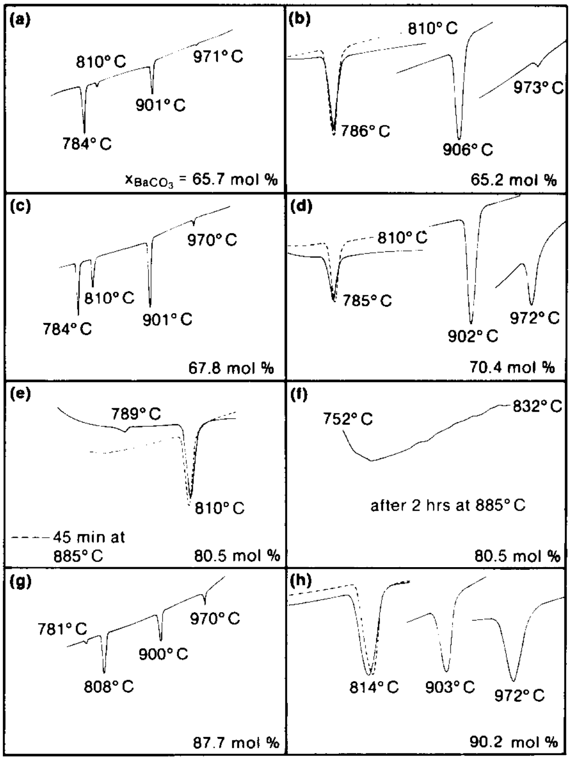

Fig. 2. DSC traces typical of K_2CO_3–$BaCO_3$ mixtures, x_{BaCO_3} greater than 65 mol%. Effects of heat treatment after incongruent melting. Not all vertical scales are the same. In (b), (d), and (h), the solid lines show traces observed in first heating, at 10 °C min^{-1}, and the broken lines are traces observed after peritectic melting and heat treatment. Other traces are explained in the text.

scale is expanded to about five times that of the other diagrams.) In Fig. 2(e) are shown two traces taken before the sample was heated to above the peritectic melting temperature. The solid curve was initially run at 10 °C min^{-1} from 750 to 830 °C prior to any heat treatment. In the broken curve, taken over the same temperature range after the sample had been held at 885 °C for 45 min, the weak eutectic feature is absent, but the $\gamma \rightarrow \beta$ peak indicated that some unassociated $BaCO_3$ was still present. The sample was then cooled to 750 °C. Figure 2(f) shows a trace characteristic of the sample's response to heating at 10 °C min^{-1}, after it had been heated to above 900 °C and then cooled to 885 °C and held for 2 h or more before being cooled to ~ 750 °C for subsequent reheating. In four repetitions of the thermal cycling for this sample, neither the eutectic nor the $\gamma \rightarrow \beta$ peaks could be distinguished from noise on the baseline. The simultaneous absence of these two peaks after annealing for two hours is substantial evidence that a coordinated compound, $K_2Ba_4(CO_3)_5$, is dominant at this concentration.

Data taken for the phase transitions are displayed in Table 1. All such

TABLE 1

Phase transitions in K_2CO_3–$BaCO_3$ mixtures

Transition	Solidus		Liquidus		Peritectic		β-$BaCO_3$ $\rightarrow$ α-$BaCO_3$	
x_{BaCO_3} (mol%)	T (°C)	Δh (arb)	T (°C)	Δh (arb)	T (°C)	Δh (arb)	T (°C)	Δh (arb)
0.0			903 ± 1	20.0				
2.2			912 ± 1	19.8				
4.1			915 ± 1	18.4				
6.0			917	18.6				
8.1		16.6	915 ± 1					
10.1	910	16.1	912 ± 1					
10.5	909 ± 1	16.4	913					
15.3	888	15.2	908					
20.2	840	14.3	896					
22.5	813	13.3	887					
23.1	817	13.0	888					
	Eutectic							
26.5	783	0.88	884					
29.0	786	2.2	870					
32.9	784	5.3	849					
33.9	783	5.6	817					
35.7	783 ± 1	7.1	833					
40.5	783	11.0	804					
41.3	784 ± 1	11.6	806 ± 3					
43.5	785	13.5						
46.3	783	12.8						
51.0	785	11.9	839 ± 2					
54.7	784 ± 1	9.7	861 ± 4					
55.1	783	9.0	860 ± 2					
57.9	785	7.6	879 ± 1					
60.4	782	6.4	889 ± 7					
63.3	782	5.5	938 ± 15		898	1.5		
65.2	784	4.1			904 ± 1	3.7	972	0.09
70.4	783	2.0			900	6.7	971	0.30
75.5	784	1.9			903 ± 2	8.3		
75.7	781	0.59			900 ± 1	7.7	969	0.44
77.7	783	1.42			899	8.3	971	0.73
	γ-$BaCO_3$ $\rightarrow$ β-$BaCO_3$							
80.5	–	–			899 ± 2	8.2	970	0.66
87.7	808	6.4			896 ± 2	4.5	969	1.1
90.2	809	7.7			899	4.1	972	1.2
96.1	807	10.0			895	1.5	968	1.4
100.0	810	13.3					975	1.8

T (°C) is the calculated temperature of onset of the leading edge of the endothermic DSC peak associated with the transition. Δh(arb) is the calculated peak area in arbitrary units. Multiplication of Δh(arb) by 1.5 gives, approximately, Δh (kJ mol^{-1}). Standard deviations for all temperatures are within ±0.5 °C unless otherwise noted.

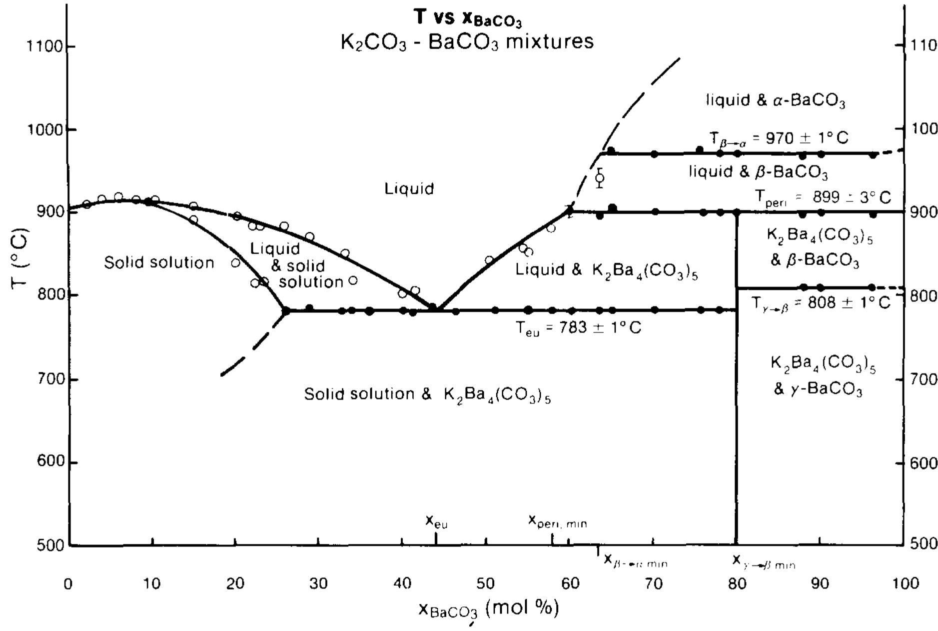

Fig. 3. Phase diagram for K_2CO_3–$BaCO_3$ mixtures.

data are the averages of at least three runs. The transition temperatures are inferred from the extrapolated peak onset temperatures determined by equipment software. The liquidus temperature, 938 ± 15 °C, given for $x_{BaCO_3} = 63.3$ mol% represents a departure from normal practice. In taking the other data, only heating runs were made since liquidus data from cooling runs are usually too variable to be of interest because of irregular supercooling. However at $x_{BaCO_3} = 63.3$ mol%, no liquidus was observed at all on heating, and cooling runs were made to try to verify that the liquidus is indeed below the temperature of the second polymorphic transition (~ 970 °C). The variation, ±15 °C, is typical of cooling run data.

The peak areas determined by the software are given as reduced enthalpies appropriate to the use of Tammann's Rule [1,4]. (Multiplication of these values for fractional molar enthalpy by a factor of 1.5 will give value approximately in kJ mol^{-1}, but the accuracy of the conversion varies with the transition.) The data in Table 1 show that the $\beta \rightarrow \alpha$ transition is at a lower and nearly constant temperature for the mixtures than for the pure $BaCO_3$ by an amount, 7 °C, which is readily resolvable by the instrument. Further studies would be needed to clarify the difference, but it seems likely that it is attributable to a narrow range of solid solution of K_2CO_3 in $BaCO_3$.

The phase diagram for these mixtures is shown in Fig. 3. The evidence for the location of the liquidus is much better for lower $BaCO_3$ concentrations, and is weak or absent for values of x_{BaCO_3} above the eutectic composition, as discussed above. In Fig. 3, the onset points, x_{eu}, $x_{peri,min}$, etc. indicated on

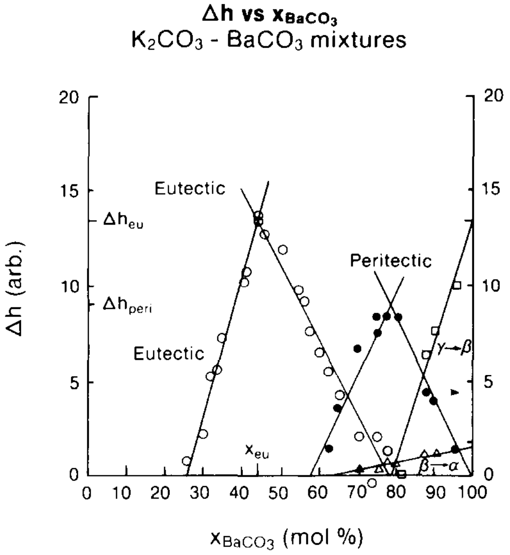

Fig. 4. Latent heats for first-order transitions in K_2CO_3–$BaCO_3$ mixtures.

the abscissa have been obtained by extrapolation from the enthalpy data.

A plot of the fractional molar enthalpy data for these mixtures is shown in Fig. 4. The descent of the eutectic line to zero at $x_{BaCO_3} = 78$ mol%, the ascent of the $\gamma \to \beta$ line from zero at $x_{BaCO_3} = 79$ mol%, and the intersection of the peritectic lines at 78 mol% are all consistent to within reasonable error with the existence of a coordinated compound $K_2Ba_4(CO_3)_5$. It is conceivable, however, the reexamination with better assessment of the concentrations would suggest instead a compound such as $K_2Ba_3(CO_3)_4$ ($x_{BaCO_3} = 75$ mol%). It does seem quite clear that the present data do not show the presence of the equimolecular compound $K_2Ba(CO_3)_2$ ($x_{BaCO_3} = 50$ mol%) reported by Le Chatelier [3]. The intersection of the eutectic lines suggests that the eutectic composition is $x_{BaCO_3} = 44$ mol%.

The straight lines which are plotted in Fig. 4 are as follows.

Eutectic (783.1 ± 1.0 °C, 82 data points)

$$\Delta h = 0.737x - 19.0 \qquad 25.8 < x \leqslant 44.0 \qquad (1a)$$

$$= -0.397x + 30.8 \qquad 44.0 \leqslant x < 78.1 \qquad (1b)$$

$\gamma \to \beta$ (808.3 ± 1.1 °C, 12 data points)

$$\Delta h = 0.647x - 51.2 \qquad 79.2 < x \leqslant 100 \qquad (2)$$

Peritectic (899.5 ± 2.7 °C, 33 data points)

$$\Delta h = 0.452x - 26.2 \qquad 57.9 < x < 78.0 \qquad (3a)$$

$$= -0.424x + 42.2 \qquad 78.0 < x < 99.4 \qquad (3b)$$

$\beta \to \alpha$ (970.20 ± 1.1 °C, 25 data points)

$$\Delta h = 0.044x - 2.8 \qquad 64 < x < 100 \qquad (4)$$

The molar enthalpy for the eutectic transition is 13.4 arbitrary units, and for the peritectic transition 9.1 arbitrary units. For the $\gamma \to \beta$ transition, the calculated molar enthalpy is 13.4 (from eqn. (2)), compared with the value observed for pure $BaCO_3$ of 13.3 arbitrary units. The calculated molar enthalpy for the $\beta \to \sigma$ transition is 1.6 arbitrary units (from eqn. (4)), as compared with the value observed of 1.8 arbitrary units for pure $BaCO_3$.

DISCUSSION

Few data points were taken at very high $BaCO_3$ concentrations because of the difficulty of characterizing the residual masses of small amounts of the K_2CO_3 reagent. In addition the number of runs increases from 3–5 at low $BaCO_3$ concentration to 25 or 30 at high $BaCO_3$ concentrations because of the care which must be taken to assure that non-equilibrium concentration differentiation does not become a problem after the sample has been heated past the temperature at which incongruent melting occurs. Clearly the $\gamma \to \beta$ transition is the least well characterized transition presented here.

It would be valuable to have further investigation of the coordinated compound which is suggested by the data presented here. The present technique of preparation requires direct use of the DTA apparatus and so is slow and yields only small quantities, and in a form difficult to remove from the crucibles without risking altering the sample. It may be important in preparing larger samples to consider not only the proper composition but also the presence or absence of a CO_2 blanket as well.

In addition to the topics for future study with samples of high $BaCO_3$ concentration, the anomalous increase in melting temperature of mixtures with very low (~ 6 mol%) $BaCO_3$ concentrations appears very interesting. Such melting is rare, but not unknown. A similar increase in melting temperatures is reported for alloys of lead and thallium [8]. The maximum temperature for these alloys is reached at $x_{Tl} = 63$ mol%. Tang and Pauling [9] present evidence that ordered lattice structure is involved for the solid solution of Pb and Tl.

It is of particular interest that a similar increase in melting temperature is reported for mixtures of Na_2CO_3 and $CaCO_3$ [10]. In that case the melting temperature at a composition x_{CaCO_3} of ~ 10 mol% occurs at about 870 ° C, about 12 ° C higher than the melting temperature of pure Na_2CO_3. An X-ray study of such mixtures might be profitable. Anomalous coloring observed in the K_2CO_3–$BaCO_3$ mixtures for low x_{BaCO_3} suggest optical studies might also be warranted.

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