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THERMAL SYNTHESIS OF SODIUM CALCIUM CARBONATE — A POTENTIAL THERMAL ANALYSIS STANDARD

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ABSTRACT

Sodium calcium carbonate — an equimolar double salt ($Na_2CO_3 \cdot CaCO_3$) never described in the literature — forms by a novel solid state reaction when intimately mixed Na_2CO_3 and $CaCO_3$ powders are heated. The thermal synthesis and the properties of this compound are evaluated by thermal analysis using an instrument yielding simultaneous DTA, TG, and EGA data. The compound forms slowly at temperatures above 300°C with no gas evolution and no weight loss. This product's X-ray diffraction pattern, unique and reproducible, is not included in the ASTM X-ray data card file. Stable at room temperature, the compound undergoes four crystal inversions in the temperature range from 390 to 450°C . Easily prepared from common laboratory chemicals, this compound may be useful as a temperature and DTA resolution standard.

INTRODUCTION

While studying thermal behavior of minerals occurring in Wyoming's Green River Formation oil shales, the U.S. Bureau of Mines found that an unknown carbonate compound formed when shortite ($Na_2CO_3 \cdot 2CaCO_3$) was heated. Complete thermal data on shortite and related oil-shale minerals will be described in a subsequent publication, but in attempting to identify this unknown carbonate we synthesized it thermally. The new compound is a previously unrecognized double carbonate, $Na_2CO_3 \cdot CaCO_3$, formed from its constituent carbonates by a thermally-induced solid-state reaction. The preparation and characteristics and the thermal properties of this double carbonate are described in this paper. The remarkable crystal inversion properties of the double carbonate suggest its use as a temperature and resolution standard for thermal analysis.

Reactions which thermally combine materials into new chemical compounds have been largely ignored in thermal analysis literature. The thermally-induced chemical reactions reported are almost entirely decomposition reactions. However,

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Nikolaev *et al.*[1] present a strong case for the value of thermal synthesis of inorganic compounds, illustrating their thesis by preparation of metal compounds of O, Cl, S, Te, and Se directly from the elements. McAdie[2,3] prepared barium and strontium zincates by thermal reaction of alkaline earth carbonates with zinc oxide. While thermal synthesis has been reported, the preparation of the sodium calcium carbonate reported here involves solid-state combination of two crystalline compounds. No previous record of solid-state synthesis at temperatures short of fusion was found in a limited search.

PREPARATION AND CHARACTERISTICS

The compound $Na_2CO_3 \cdot CaCO_3$ is prepared by heating a powder mixture of the constituent carbonates. Powdered $CaCO_3$ (low in alkalies) and anhydrous

TABLE 1

X-RAY DIFFRACTION SPACINGS FROM Na_2CO_3, $CaCO_3$ AND $Na_2CO_3 \cdot CaCO_3$

[a]$CaCO_3$		[b]Na_2CO_3		$Na_2CO_3 \cdot CaCO_3$	
2θ (°)	I/I_1	2θ (°)	I/I_1	2θ (°)	I/I_1
				14.3	59
				15.1	3
				16.8	7
		19.8	2	20.2	66
		21.5	1	21.4	16
23.0	12	22.8	3		
		23.6	5	25.0	9
		26.2	13	25.6	18
29.4	100	27.7	16	29.0	19
				29.8	100
		30.2	100	30.4	21
31.4	3	33.1	28	31.1	11
		34.6	55	35.1	7
36.0	14	35.3	69	35.6	74
				36.2	32
		38.1	90	36.8	7
39.4	18	40.0	45	39.1	11
		41.4	55	41.3	15
		42.4	10	42.0	38
43.1	18			43.1	4
		44.6	15	44.1	45
		46.6	33	45.2	25
47.1	5			47.0	26
47.5	17	48.3	34	47.9	6
48.5	17	50.8	5	51.4	20
		53.6	17	55.6	11
56.5	4	54.6	15	56.1	10
57.4	8			57.0	8
				58.0	7
				60.4	4

[a]ASTM card 5-0586. [b]Similar to ASTM card 19-1130.

Na_2CO_3, each meeting American Chemical Society reagent grade specifications, were used in our experiments. The mixture of sodium and calcium carbonates is prepared by stirring together equimolar weights of the two carbonate powders. If the carbonate mixture is ground before heating, the reaction goes faster.

X-ray diffraction examination of the carbonate mixture is needed to demonstrate that a combination occurs. All X-ray data reported on heated samples were obtained after cooling them to room temperature. As a sample of the carbonate mixture is heated, the X-ray diffraction patterns of the two separate carbonates gradually disappear and an entirely new pattern replaces them. Table I gives the diffraction angles in degrees 2θ for the two constituent carbonates, comparing them with the angles of the new pattern. Each of the diffraction angles is accompanied by a value for relative intensity of that particular reflection compared to the strongest reflection of the pattern arbitrarily set at 100. Patterns of the $CaCO_3$ and Na_2CO_3 starting materials are virtually identical with the starred patterns for calcite and sodium carbonate in the ASTM X-ray data card file. The pattern for the $Na_2CO_3 \cdot CaCO_3$ product is not included in the extensive ASTM listing through 1969 (card set 19). To illustrate how different the new pattern is from the patterns of its constituents, Fig. 1 compares them, plotting diffraction angles and relative line intensities for the constituents and the product.

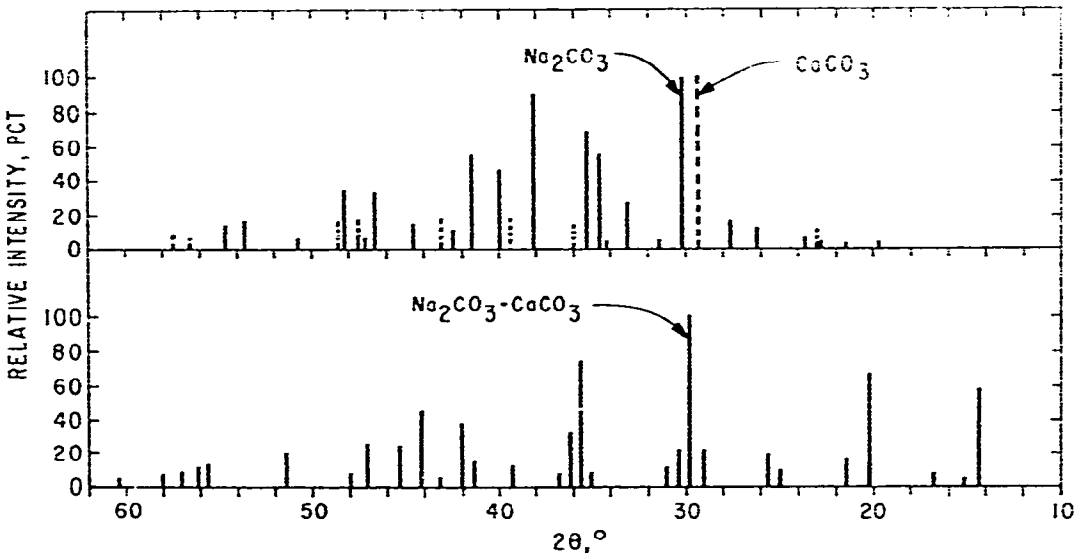

Fig. 1. X-ray diffraction patterns of the mixed carbonates and the double carbonate compound.

In the unheated mixture X-ray diffraction detects only the starting carbonates, and no change is detected when the sample is heated at or below 300 °C. Some combination occurs by heating to 350 °C, but the reaction is slow. Higher temperatures (to 500 °C) hasten the reaction and longer residence times (for instance, overnight) carry it further toward completion. Eventually the X-ray patterns of the component carbonates vanish, leaving only the new pattern. If the initial mixture contains a

sufficient excess of either carbonate component, this carbonate remains detectable by X-ray diffraction in addition to the double carbonate formed during heating.

When the sodium calcium carbonate compound is heated above 600°C (750°C in CO_2), decomposition begins. Carbon dioxide is evolved, and TG shows a weight loss. After this decomposition is complete, X-ray diffraction detects Na_2CO_3 and CaO in the still unmelted powder. Heating this mixture to still higher temperatures (above 850°C) eventually fuses the sodium carbonate.

The original powder does not change in physical appearance with formation of the double carbonate. No shape change indicating melting occurs in the mixture below the fusion point of Na_2CO_3. Although the powder sinters slightly, a finger touch restores the powder form. A crude specific gravity measured on the compound was 2.6, midway between calcite at 2.71 and sodium carbonate at 2.51. The compound does not separate appreciably when suspended in mediums near 2.6; it either sinks or floats.

Atmosphere over the reaction carbonates apparently exerts no influence on the solid-state combination reaction. The double carbonate has been prepared under the following atmospheres: air, N_2, CO_2, and He, with no evident change in behavior.

Shape of the container holding the reacting powders is apparently of no importance. A crucible in a muffle furnace is just as satisfactory as the flat-pan sample holder of the Bureau of Mines thermal analysis apparatus (Johnson and Smith[6]) or the deep-well holders used frequently in thermal analysis.

The ASTM X-ray data card file lists a diffraction pattern for a sodium calcium compound, also $Na_2Ca(CO_3)_2$, as card 2-970. We duplicated this pattern by heating the hydrated carbonate mineral gaylussite ($Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$) to 200°C and running X-ray diffraction on the cooled product. When this sample was heated to 500°C, its X-ray diffraction pattern changed to that given in Table I for the double carbonate. The sodium calcium carbonate yielding the Table I pattern is stable or at least metastable at room temperature. Deterioration in prepared samples has not been detected during short term storage prior to consumption in other testing.

THERMAL ANALYSIS

Formation of the double carbonate and the thermal effects of the crystal inversion characteristics it exhibits were evaluated by thermal analysis. The apparatus used in this study was developed by the U. S. Bureau of Mines especially for evaluating the thermal behavior of naturally-occurring solid fuels like oil shales and coals (Smith and Johnson[4]). This apparatus generates continuous, simultaneous DTA–TG–EGA readings during thermal analysis of a single sample (Smith and Jonhson[5,6]). While the specific abilities of this apparatus are not vital to thermal synthesis of the double carbonate, the DTA, TG, and EGA data outputs shown on subsequent plots were actually obtained simultaneously on a single sample.

The thermal analysis results in Fig. 2 show two features bearing on formation of the double carbonate. Heated at a rate of 10°C/min, these are the first and second

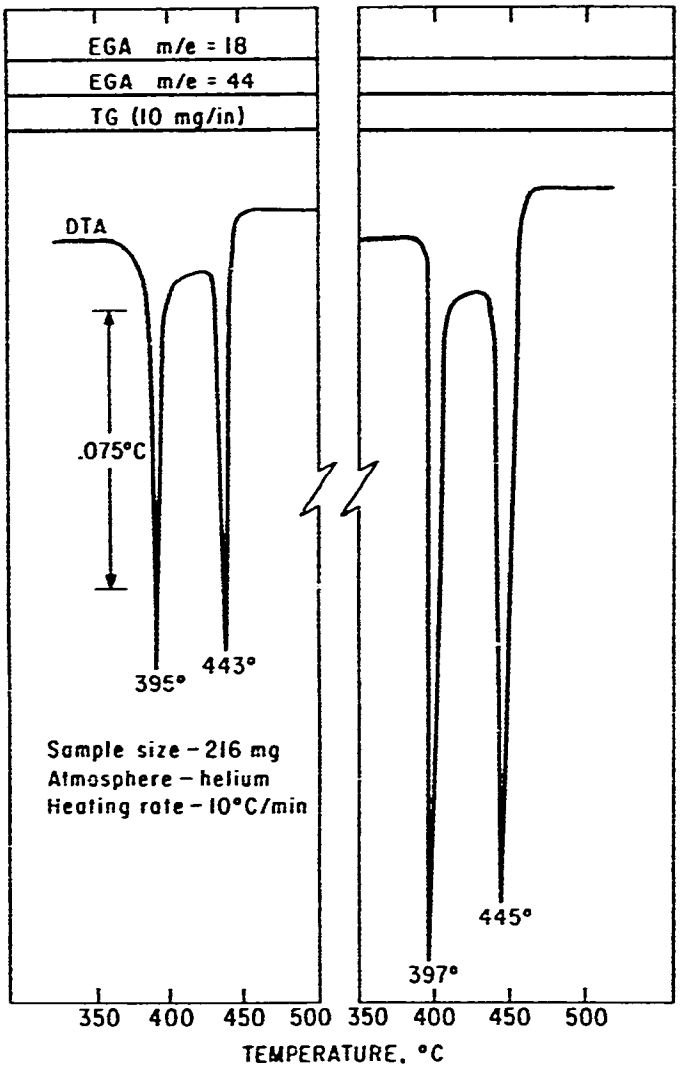

Fig. 2. Successive thermal analyses of reacting carbonate mixture.

runs on one sample of the sodium carbonate–calcium carbonate mixture. The two endothermic DTA peaks shown are crystal inversions characteristic of the sodium calcium carbonate compound. The first noteworthy point is that in the second run these peaks are about 65 percent larger than in the first run, indicating that significantly more of the inverting compound has formed and is responding in the second heating. This illustrates the continuing nature of the reaction.

The second point significant to double carbonate formation in Fig. 2 is the complete absence of weight change or gas evolution during both heating cycles. The TG output is a flat line at a sensitivity of 10 mg/in on a 12-in chart. The extremely sensitive mass spectrometric EGA outputs for CO_2(m/e=44) and H_2O(m/e=18) are correspondingly flat. During these runs the mass range from 14 to 50 was scanned continuously with no response. Over the entire temperature range where synthesis of

the compound giving the new-X ray diffraction pattern and the crystal inversions must have occurred, no weight is gained or lost, and no gas is evolved.

At a slower heating rate the double carbonate compound demonstrates a group of four crystal inversions by DTA. Fig. 3. shows the DTA response of the double

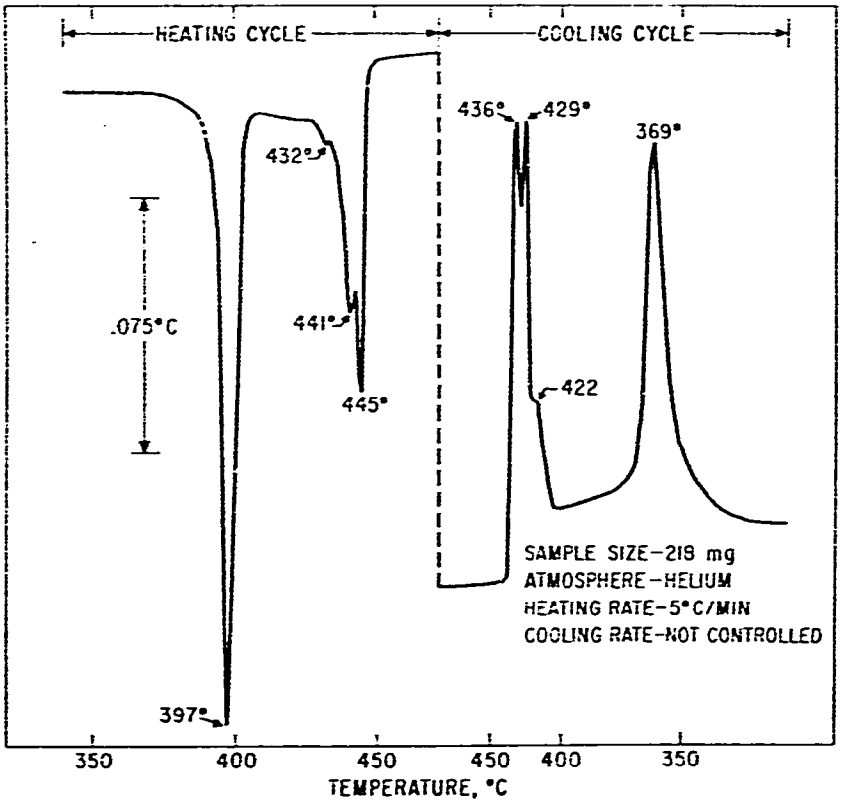

Fig. 3. Crystal inversions of $Na_2CO_3 \cdot CaCO_3$.

carbonate during successive heating and cooling. In this sample only the double carbonate was detectable by X-ray diffraction. The four separate endothermic reactions apparent on the heating curve are presented as exotherms in reverse order on the cooling curve. The heating rate used to produce Fig. 3 was 5°C/min, half that which produced only two endothermic peaks in Fig. 2. The cooling rate was not controlled, explaining shape differences between the heating and cooling DTA curves. Temperatures given for the inversion peaks and the one incompletely resolved shoulder were obtained on our carefully calibrated thermal analysis instrument. These temperatures are reproducible under duplicate conditions within one or two degrees centigrade. On the original tracings the areas under the comparable heating and cooling peaks were very nearly identical. For presentation purposes the DTA line was broken between the heating and cooling curves in Fig. 3.

The crystal inversion behavior of the double carbonate is repeatable cycle after cycle. Each repeat run generates the four inversions on heating and cooling

under the conditions indicated in Fig. 3. On repeat runs the DTA curves do not change significantly in size once the X-ray diffraction pattern shows disappearance of Na_2CO_3 and $CaCO_3$.

DISCUSSION

Heat-induced formation of a chemical compound by a solid-state reaction is indicated by the experimental evidence. Development of a new X-ray diffraction pattern as those of the two component carbonates disappear points strongly to this. The new pattern appears without loss of weight or evolution of gas. An excess of either constituent can be detected after the new compound is formed. The equation below must represent the chemical reaction which occurs:

$$Na_2CO_3 + CaCO_3 \rightarrow Na_2Ca(CO_3)_2 \qquad (1)$$

Mechanism of the compound's formation offers a puzzle. In the absence of fusion the formation of an equimolar compound appears unlikely, yet it forms. Equilibrium for the reaction expressed in equation 1 must be very strongly toward the product side, because the compound continues to form until the initial carbonates are no longer detectable by X-ray diffraction. Higher temperatures encourage the reaction, but at best the reaction is leisurely. Slowness of the reaction explains why no heat of formation could be detected by DTA. This slowness coincides with the obvious difficulty of making an equimolar compound from randomly distributed crystalline constituents. Available evidence points to a heat-induced solid-state combination reaction between the two carbonate components. This solid-state reaction is certainly novel, warranting further study.

The nature of the mixed carbonate formed is unknown at present. The series of techniques used by Garcia-Clavel *et al.*[7] in studying double alkaline earth carbonates seems particularly appropriate and is being applied to this study. Preliminary IR data verify formation of a new compound.

Four readily repeatable crystal inversions in a temperature span near 50°C indicate a temperature-sensitive compound bent on reorganizing. None of the available data offers the slightest hint that the DTA endotherms shown in Figs. 2 and 3 are not crystal inversions. Different heat capacities for the materials existing below, between, and above the two endothermic peaks are indicated by the shifts in DTA baseline indicated in Fig. 2. The same baseline shifts also appear in the better-resolved DTA trace in Fig. 3. These strong shifts point to sharply different heat capacities for the compounds existing on the high and low sides of the crystal inversions. High-temperature X-ray diffraction looks like the best approach to evaluating the nature of these inversions.

Sodium calcium carbonate might serve as a standard compound for thermal analysis. Four temperature inversions occurring between 380 and 450°C should adequately mark temperatures for any apparatus over this range. Three of these inversions occur in the temperature range 412–573°C for which McAdie[8] requested

recommendations of suitable systems. This compound might also be used to check resolution of DTA systems as indicated by the markedly improved resolution we achieved by halving the heating rate (compare Figs. 2 and 3). Sodium calcium carbonate can be easily, cheaply, and conveniently prepared from ubiquitous laboratory chemicals. Its DTA inversion responses are relatively weak, approximately on the order of the alpha-to-beta quartz inversion, but should be detectable by most instruments.

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