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Figure 1: Fig. 2. Calculation diagrams for X-ray powder patterns of anhydrous sodium carbonate

Abstract

Full Text

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NEW DATA ON THE POLYMORPHISM OF SODIUM CARBONATE*

(Presented by Academician I. I. Chernyaev, 10 VI 1957)

Jaffé and Marten (^{1}), using methods of thermography, dilatometry, and electrical conductivity, established that anhydrous sodium carbonate has two polymorphic transformations: at 360 and 480°. According to X-ray diffraction analysis, the crystal structure of Na_2CO_3 changes only at 480°; at 360° the authors observed no structural changes.

Fig. 2. Calculated diagrams of X-ray powder patterns of anhydrous sodium carbonate:
a –α-Na_2CO_3 –low-temperature modification; the X-ray pattern was obtained at room temperature;
b –β-Na_2CO_3 –at 350°;
c –γ-Na_2CO_3 –at 500°;
d –δ-Na_2CO_3 at 566°.

A. I. Lazareva (^{2}) also noted, on differential heating curves of Na_2CO_3, endothermic effects corresponding to phase transitions at 340–350 and 470–475°.

We carried out an X-ray diffraction and thermographic study of the process of polymorphic transformations of anhydrous sodium carbonate as a function of temperature and of the preceding history of the specimen.

For the study, sodium carbonate of the "Beker' s Analysed" grade, composition 99.78% Na_2CO_3, was used.

X-ray diffraction analysis was carried out by the powder method in a cylindrical camera specially adapted for obtaining X-ray photographs at different temperatures. The construction of such a camera and the method of investigation were described by V. G. Kuznetsov (^{3}). Before X-ray photographing, the initial Na_2CO_3 was melted in a platinum crucible at a furnace temperature of 860-880°. The remelted sodium carbonate was ground in an agate mortar to a pow-

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[*] E. S. Kovaleva took part in the experimental work.

der, with a grain size of approximately 10^{-4}–10^{-5} cm. Then the substance was placed in an open thin-walled quartz capillary 0.5-0.7 mm in diameter. Before irradiation the salt was kept for 45-60 min at a strictly definite temperature, after which, at this same temperature, X-ray photographing was carried out with unfiltered iron radiation, with an exposure of 3-4 hours and rotation of the specimen. X-ray photographs of the powders were obtained from one and the same specimen successively at the temperatures: room temperature, 80, 102, 122, 164, 204, 244, 350, 402, 450, 500, 566°, and again room temperature. Each time the specimen was heated from room temperature to the specified temperature. The results obtained, summarized in Tables 1 and 2 and in Figs. 1 and 2, show that Na_2CO_3 in the temperature interval from room temperature to melting exists

Table 1

Phase state of Na_2CO_3 as a function of temperature according to X-ray diffraction data

Temperature, °C	room	80	102	124	164	204	244	350	402	450	500	566
Phase	α	α	α	α	α	α	α	β	β	β	γ	δ
Phase	α											δ

Table 2

Values of interplanar spacings (d) and relative intensities (I) of X-ray lines of the α-, β-, γ-, and δ-modifications of Na_2CO_3

α-Na_2CO_3*, room temperature		β-Na_2CO_3, $t =$ 350°		γ-Na_2CO_3, $t =$ 500°		δ-Na_2CO_3, $t =$ 566°		α-Na_2CO_3*, room temperature (t)		β-Na_2CO_3, $t =$ 350°		γ-Na_2CO_3, $t =$ 500°		δ-Na_2CO_3, $t =$ 566°	
I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d
1	4.73	4	3.43	7	3.55	5	4.16	4	1.46	3	1.235			3	1.066
2 diff.	3.74	6	3.09	8	3.18	5	3.81	1	1.42					diff.	
3	3.003	9	2.65	6	2.90	2	3.57	4	1.384	4	1.205			5 diff.	0.985
8	2.92	7	2.59	9	2.64	7	3.33	2	1.341	diff.					
2	2.68	8	2.45	4	2.54	7	2.96	3	1.288	2	1.052				
8	2.60	5	2.35	7	2.19	1	2.88	4	1.269	1	1.098				

Reproductions of X-ray powder diffraction patterns labeled , , , , .

Figure 2: Reproductions of X-ray powder diffraction patterns labeled , , , , .

α-Na_2CO_3*, room temperature		β-Na_2CO_3, $t =$ 350°		γ-Na_2CO_3, $t =$ 500°		δ-Na_2CO_3, $t =$ 566°		α-Na_2CO_3*, room temperature (t)		β-Na_2CO_3, $t =$ 350°		γ-Na_2CO_3, $t =$ 500°		δ-Na_2CO_3, $t =$ 566°	
7	2.54	8	2.19	5	2.10	9	2.66	2	1.245	diff.					
8	2.34	4 dbl.	2.08	5	1.93	2	2.49	2	1.223	1	1.089				
5	2.24	6	1.96	6	1.89	4	2.39	6	1.190	2	1.081				
6	2.16	6	1.90	2	1.82	8	2.15	2	1.154	6	1.061				
3	2.02	1	1.83	1	1.77	5	2.06	4	1.095	1	1.029				
6	1.94	5	1.75	4	1.71	1	2.01	3	1.085	6	1.013				
7	1.87	5	1.69	3	1.590	7	1.87	3	1.077	2	0.994				
		3	1.64	4 diff.	1.510	5	1.72	2	1.070	1	0.980				
		4	1.58	5 diff.	1.305	2	1.63	6	1.057						
2	1.79	5	1.53	2 diff.	1.239	3	1.58	3	1.051						
4	1.70	1	1.51	2 diff.	1.194	5	1.51	2	1.039						
4	1.67	4	1.48	1	1.077	2	1.48	diff.							
3	1.62	3	1.405	4	1.005	4	1.385	2	1.034						
		2	1.183	1	1.983	5	1.308	diff.							
4 dbl.	1.57	5	1.314			1	1.214	6	1.010						
4 dbl.	1.52	5	1.285			5	1.170	4	1.002						
4	1.49	1	1.251			1	1.117	dbl.	0.993						
4	1.48							3 diff.	0.985						
								3	0.973						

* Annealing at 200°, 7 days.

Fig. 1. Reproductions of X-ray diffraction patterns of powders of four modifications of anhydrous sodium carbonate: **a** –α-Na_2CO_3; the X-ray diffraction pattern was obtained at room temperature in an ordinary cylindrical X-ray cam-

Fig. 3

Figure 3: Fig. 3

era; the specimen was annealed first at 120° for 22 h, then at 200° for 173 h; **b** – α-Na_2CO_3; the X-ray diffraction pattern was obtained at room temperature in a high-temperature camera from the specimen after X-ray photography at 566°; **c** –β-Na_2CO_3; the X-ray diffraction pattern was obtained at 350°; γ-Na_2CO_3, at 500°; δ-Na_2CO_3, at 566°.

not in two crystalline forms, as has hitherto been believed, but in four, each phase having its own characteristic structure, namely: $\alpha = Na_2CO_3$–the low-temperature modification (Figs. 1a, 2a); $\beta = Na_2CO_3$–the form existing above 350° (Figs. 1b, 2b); $\gamma = Na_2CO_3$–above 485° (Figs. 1c, 2c); and $\delta = Na_2CO_3$ –above 566° (Figs. 1d, 2d).

The results presented are in agreement with the data of a thermographic study, which are given below.

Fig. 3. Heating curves of Na_2CO_3 after: **a**–melting of the salt; **b**–storage for about a year in a jar with a ground-in stopper; **c**–storage for more than a year in air under laboratory conditions; as a result of absorption of moisture from the air, Na_2CO_3 was converted into $Na_2CO_3 \cdot H_2O$

Differential thermographic analysis was carried out on an N. S. Kurnakov pyrometer. Platinum-platinum-rhodium thermocouples were used. The resistance in the circuit of the simple thermocouple was 17,000 ohms, and that of the differential thermocouple was 1,000 ohms. Calcined Al_2O_3 served as the standard for the differential recording. Heating curves of Na_2CO_3 were recorded for samples with different prior histories.

Table 3

Temperatures of phase transitions of Na_2CO_3 as a function of the preceding history of the sample

Sample No.	Prior history of the sample	Dehydration of $Na_2CO_3 \cdot H_2O$	[[unclear: column heading]]	Transition $\alpha \to \beta$	Transition $\beta \to \gamma$	Transition $\gamma \to \delta$	Melting of salt
1	Remelted or dried at 140°	–	–	350	475	588	850

Sample No.	Prior history of the sample	Dehydration of $Na_2CO_3 \cdot H_2O$	[[unclear: column heading]]	Transition $\alpha \to \beta$	Transition $\beta \to \gamma$	Transition $\gamma \to \delta$	Melting of salt
2	Calcined at 500°, 2 hours	–	–	350	485	620	850
3	Sample No. 2 after three days' storage in a desiccator	–	–	350	480	630	850
4	Calcined at about 650°, 2 hours	–	–	350	485	–	850
5	Stored for about a year in a jar with a ground-in stopper	–	185	340	470	560	850

Sample No.	Prior history of the sample	Dehydration of $Na_2CO_3 \cdot H_2O$	[[unclear: column heading]]	Transition $\alpha \rightarrow \beta$	Transition $\beta \rightarrow \gamma$	Transition $\gamma \rightarrow \delta$	Melting of salt
6	Stored for more than a year openly in air	80— 12095— 109	245	350	455	585	850
Literature data	Literature data	80— 12095— 109—	245——	350340350360	455470475480	585	850850 (*)850850 (1)

As is evident from Table 3 and Fig. 3, the thermograms of all the investigated Na_2CO_3 samples reveal not only the previously known thermal effects characterizing phase transitions at 340–360 and 470–485°, but also an endothermic effect at 560–588 or 620° (depending on the treatment of the sample), corresponding to a third polymorphic transformation of sodium carbonate, previously undescribed in the literature, from the γ- to the δ-form. This phase transition of Na_2CO_3 was first established by us by the X-ray powder method during X-ray photography in a high-temperature chamber and was described above. The observed discrepancy between the temperatures of the phase transformations according to X-ray and thermographic data is apparently caused by the different heating rates of the substance, different grain size, and also by the previous history of the sample.

Thus, as a result of the present investigation, new data have been obtained on the polymorphism of anhydrous sodium carbonate. By X-ray and thermographic methods it has been established:

1. The existence of Na_2CO_3 in the temperature interval from room temperature to melting in four crystalline forms:
   a) α-Na_2CO_3—a low-temperature modification that exists up to 340–350°;
   b) β-Na_2CO_3—exists in the temperature interval from 340–350 to 470–485°;
   c) γ-Na_2CO_3—exists within the limits from 470–485 to 565–620°;
   d) δ-Na_2CO_3—a high-temperature modification existing above 560–

620°.

The temperature range of existence of the phase depends on the treatment of the sodium carbonate samples.

2. A change in the crystal structure during the phase transition from the α- to the β-form at 340–350°.

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Note: Figure translations are in progress. See original paper for figures.