To the Problem of the Formation of Modifications of Calcium Oxide

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Calcium oxide does not undergo any modification changes at temperatures 590 and 700°C and only a simple thermal expansion takes place.

There exist many papers supporting the existence of various modifications of calcium oxide as deduced from certain anomalies of CaO at 405—410°C [1], from deviations on DTA curves obtained in heating CaO to 425°C [2, 3], from endothermic effect observed at 442°C, caused by α CaO—β CaO transition [4], or from the change of the slope of the electrical conductivity curve for CaO at 527°C [5] or 680°C [6], respectively. On the other hand many papers point out that in the case of CaO no changes of the structure type occur at high temperatures and only the interplanar spacings [7, 8] are changed as a consequence of the thermal expansion of a substance [9], while the X-ray spectra at heating CaO to 650, 900, and 1500°C are identical [10]. At sintering CaO to 876°C no changes have been observed [11]. In recent work [12] in which the author deals with the properties of CaO at high temperatures, the following statements can be found:

1. CaO undergoes the modification changes in the temperature range from 20—1000°C (endothermic effects between 470—490°C and 700—715°C), found by DTA.
2. These changes are reversible but not instant.
3. It has been proved by the X-ray analysis at 550—720°C that these thermal effects are probably caused by the cubic/tetragonal transformation of CaO.
4. These changes probably cause the increased chemical reactivity about 500°C as well as the change of electrical conductivity.

Since we have not come across similar effects in our investigation, we consider it useful to publish our data.

Experimental

Calcium oxide was obtained after heating the precipitated calcium carbonate anal-grade for 2 hours at 1000°C.

Spectral analysis of $CaCO_3$ is as follows: Si 0.005—0.01%; Al 0.01—0.05%; Mg 0.1—0.5%; Sr 0.001—0.005%; Fe 0.005—0.01%; Mn 0.001—0.005%; Na 0.05—0.1%.

All samples were examined by powder method.

X-ray diffraction analysis of calcium oxide at temperatures 20, 590, and 700°C was carried out in a high-temperature camera UNICAM. The accuracy of temperature measurement was ± 5°C. The sample of CaO was placed in a quartz capillary. CuK_α radiation was used. The furnace was evacuated to $5 \cdot 10^{-3}$ Torr. At the end of heating the same sample was investigated again at 20°C.

Table 1

No.	d_{hkl} [Å]	I/I_0	*hkl*
1	2.7471	37	111
		12 (β)	
2	2.3792	100	200
		31 (β)	
	1.6892	52	220
		19 (β)	
4	1.4417	17	311
5	1.3815	18	222
6	1.1967	4	400
7	1.0993	5	331
8	1.0735	3	420
9	0.97911	3	422
10	0.92300	3	511, 333
11	0.84865	2	440
12	0.81145	2	531
13	0.80016	3	600, 442

Table 2

	d_{hkl} [Å]			
No.	20°C	590°C	700°C	20°C
1	2.7471	2.7669	2.7719	2.7471
3	2.3792	2.4025	2.4162	2.3804
5	1.6892	1.7035	1.7043	1.6886
14	1.0735	1.0803	1.0858	1.0722
15	0.97911	0.98802	0.98857	0.97911
21	0.81145	0.81813	0.81925	0.81153
23	0.80016	0.80667	0.80761	0.79916

Table 3

t [°C]	a [Å]
20	4.795 ± 0.003
590	4.825 ± 0.002
700	4.832 ± 0.003
20	4.796 ± 0.003

The powder diffraction data for CaO (20°C) and the values d_{hkl} [Å], I/I_0, and *hkl* are compiled in Table 1.

Mean values of the interplanar spacings d_{hkl} were calculated from 10 measurements for each line, while the correction of the film shrinkage was taken into account. The changes of d_{hkl} at temperatures 20, 590, 700°C and again 20°C (after cooling the sample)

are given in Table 2 for the most important lines. Intensities are not presented as they have not been changed with temperature increase of the sample. Mean values of the lattice constants were determined at temperatures 20, 590, 700, and 20°C (Table 3). The lattice constants were computed from all lines from 10 measurements for each line.

Discussion

The X-ray diffraction analysis of CaO at high temperatures points at the thermal expansion (Table 2); the cubic symmetry is not changed with temperature increase. The relative intensities of individual lines of CaO do not change with increasing temperature. It follows from this that no modification changes take place.

Calcium oxide does not undergo any changes at temperatures 590 and 700°C and only a simple thermal expansion occurs.

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