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⑥ New High Pressure Form of Calcium Disilicide,

⑩ by

M. S. Silverman and J. R. Soulen.

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PENNSALT CHEMICALS CORPORATION
Research and Development Department
Wyndmoor, Pennsylvania

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NEW HIGH PRESSURE FORM OF CALCIUM DISILICIDE

By M. S. Silverman and J. R. Soulen

Research and Development Laboratories

Pennsalt Chemicals Corporation

Wyndmoor, Pennsylvania

Calcium disilicide is known to have a hexagonal layer type structure¹ as do graphite and boron nitride. At very high pressures and

(1) J. Böhm and O. Hassel, Z. anorg. u. allgem. Chem., 160, 152 (1927).

temperatures the latter compounds form the more dense cubic polymorphs, diamond² and borazon.³ CaSi_2 has ~~now~~ been transformed at high

(2) F.P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Jr., Nature, 176, 51 (1955).

(3) R. H. Wentorf, Jr., J. Chem. Phys., 26, 956 (1957).

pressures to a new, more dense modification which appears to be tetragonal.

Commercial grade CaSi_2 obtained from K and K Laboratories was used as one starting material. This contained several percent iron

as an impurity. Mixtures of semiconductor grade silicon, spectroscopic grade graphite, and CaO prepared by heating 99.9 % CaCO_3 were also used.

The apparatus was of the tetrahedral anvil type developed at the National Bureau of Standards.⁴ The sample holder, heating

(4) E. C. Lloyd , U. O. Hutton and D. P. Johnson, J. Res. N. B. S., 63C, 59 (1959).

assembly, and calibration techniques were similar to those described previously,⁵ except that a boron nitride insulating capsule was used

(5) J. R. Soulen and M. S. Silverman, J. Polymer Sci., 1, 823 (1963).

between the graphite heater and the sample.

In carrying out the runs, CaSi_2 or a $\text{CaO} + \text{Si} + \text{C}$ mixture was first compressed to the desired pressure between 8 and 87 kilobars, temperature was then raised and held at the desired level, which ranged up to 1800° . After 2 to 10 minutes the electrical power was shut off and the sample was decompressed after the product had reached ambient temperature.

With CaSi_2 as the starting material, striking changes were noted in the solid resulting from a number of runs. Under microscopic examination it appeared

that essentially 100% conversion to a reflective, coral material had occurred from the original grey form. In concentrated HCl the latter reacted with vigorous effervescence whereas the new form, even when finely ground, underwent only slight reaction. Density of the hexagonal starting material was $2.47 \pm 0.02 \text{ g/cm}^3$, in good agreement with 2.46 g/cm^3 reported previously.¹ Measured densities of the high pressure form ranged from 2.60 to $2.76 \pm 0.02 \text{ g/cm}^3$. The highest value was obtained from a product formed under the most severe combination of conditions, 87 kilobars and 1500° , and thus must be closest to correct for the new form. X-ray diffraction films of many of the samples gave an identical powder pattern which is characteristic of the new form and is completely different from that of the original material. The strongest lines are listed in Table I.

These can be indexed on the basis of a tetragonal structure with $a = 6.23 \text{ \AA}$ and $c = 4.52 \text{ \AA}$. Density calculated from these constants, assuming 3 CaSi_2 per unit cell, is 2.73 g/cm^3 , compared with 2.76 for the highest density product. Taking the iron impurity into account, product analysis showed about 2.6% Fe, and a composition approximately $\text{Ca}_{0.93}\text{Fe}_{0.05}\text{Si}_{2.00}$. Assuming simple substitution of Fe for Ca to this extent in the proposed CaSi_2 structure, calculated density is 2.75 g/cm^3 , in excellent agreement with the measured value.

To determine whether iron is a necessary constituent of the new structure, reaction of calcium oxide, silicon and carbon was carried out under high pressure conditions using very pure reactants. Although conversions were poor, the X-ray diffraction powder pattern of Table I was obtained from a number of the pressed pellets, showing formation of the new high pressure form from these entirely different reactants in which the impurity level is very low. The pattern must thus be characteristic of calcium disilicide itself, and the presence of iron in the products obtained from impure CaSi_2 is not essential to obtain it.

The high pressure form was obtained from hexagonal CaSi_2 in varying amounts over the ranges 17 to 87 kilobars and 700° to 1800° . Below 17 kilobars no transformation occurred, even at temperatures up to 1500° . Besides thermodynamically favoring the reaction, pressure also favors formation of the new form kinetically. Thus in 10-minute runs at 1250° and 17 and 42 kilobars, conversions to the high pressure form were less than 50% and 100%, respectively. At 1000° no new product was obtained after 10 minutes at 20 kilobars whereas complete conversion resulted after 10 minutes at 50 kilobars and 3 minutes at 83 kilobars. To obtain essentially complete conversion to the high pressure form in short periods of time, pressures above 40 kilobars and temperatures above 1000° are required simultaneously.

The authors wish to thank Dr. W. Clavan and Mr. R. Hamilton for obtaining the X-ray diffraction patterns, and the analytical

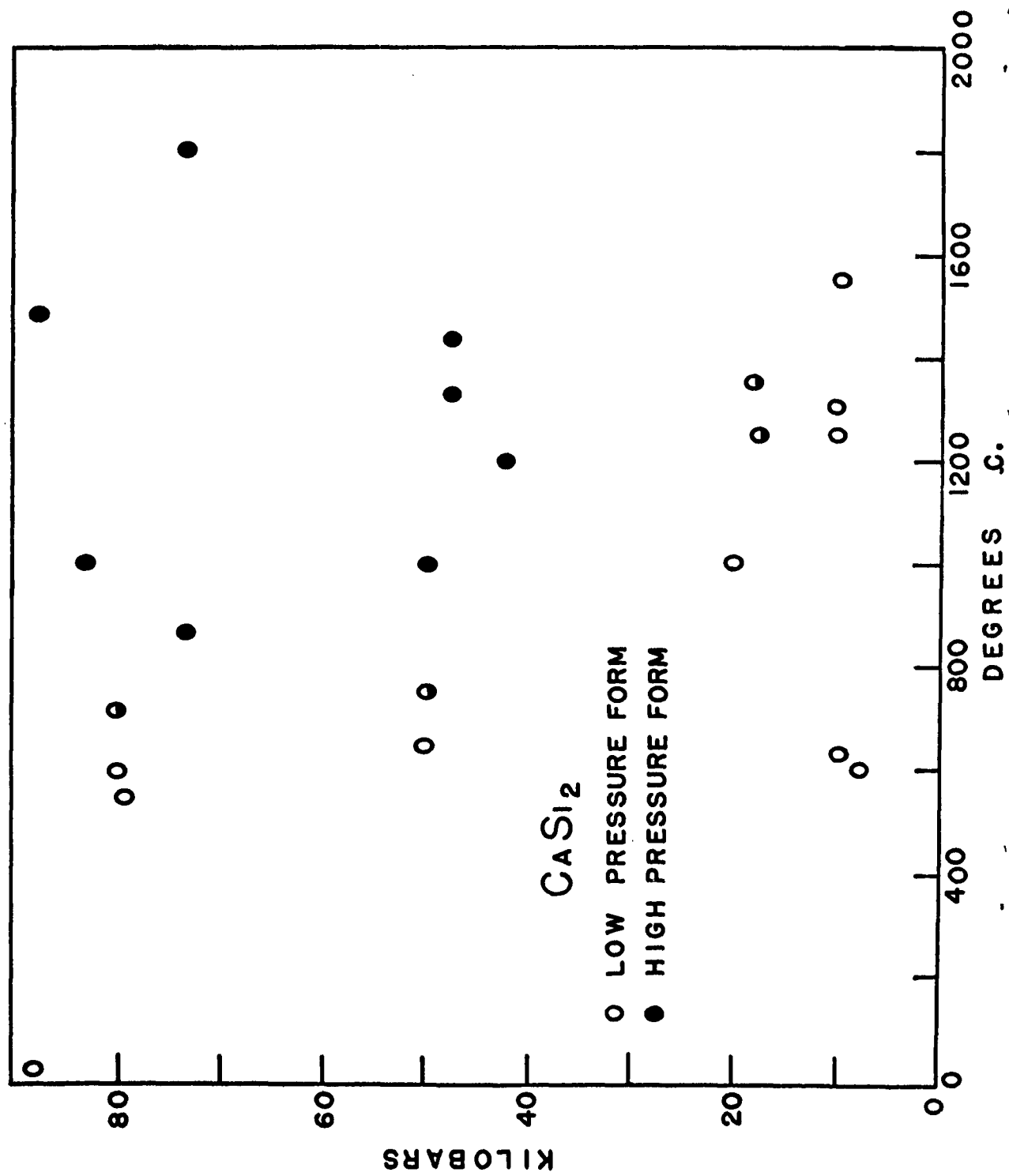
and shop groups for their help in this work. It was supported in part by the Office of Naval Research.

TABLE I. X-RAY POWDER DIFFRACTION PATTERN OF HIGH PRESSURE
FORM OF CALCIUM DISILICIDE

$d(\text{\AA})^a$	I	hkl	$\sin^2 \theta$	
			obsd.	calc. ^b
2.77	100	210	.0774	.0766
2.28	80	002	.1143	.1164
2.14	55	102	.1297	.1317
1.76	55	212	.1918	.1929
1.56	50	$\left\{ \begin{array}{l} 222 \\ 400 \end{array} \right.$	.2442	$\left\{ \begin{array}{l} .2388 \\ .2450 \end{array} \right.$
1.512	30	$\left\{ \begin{array}{l} 302 \\ 410 \end{array} \right.$	.2599	$\left\{ \begin{array}{l} .2542 \\ .2603 \end{array} \right.$
1.326	30	$\left\{ \begin{array}{l} 213 \\ 421 \end{array} \right.$	.3380	$\left\{ \begin{array}{l} .3387 \\ .3353 \end{array} \right.$
1.235	25	223	.3896	.3843

a Copper K_{α} radiation taken as $1.5418 \text{ \AA}$.

b Assuming tetragonal structure with $a = 6.23 \text{ \AA}$ and $c = 4.52 \text{ \AA}$.



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