

An X-ray study of ionic carbide solid solubilities

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Calcium carbide and its combination with sodium carbide, lithium carbide and cerium carbide were studied via X-ray diffraction to determine the solid solubilities of these latter carbides in calcium carbide. No solid solubility of sodium or lithium carbide in calcium carbide was found but cerium carbide appears to be soluble up to approximately 40 mol% in CaC_2 .

1. Introduction

CaC_2 is a technically important material used both in the production of acetylene and steel making [1, 2]. CaC_2 has four distinct crystal structures. The structures of these polytypes have been extensively studied [3-5]. CaC_2 (I) is body centred tetragonal and stable between 0 and 450°C, with $a = 5.49 \text{ \AA}$ and $c = 6.38 \text{ \AA}$. The structure of this form is well established [3, 6, 7] but there is no widespread agreement about the other three polytypes. According to Stackelberg and Vannerberg [3, 4, 5], CaC_2 (II) is tetragonal or monoclinic and is metastable at room temperature but stable below 0°C. CaC_2 (III) is either triclinic or tetragonal and is only metastable [3, 4]. CaC_2 (IV) is stable above 450°C and is face centred cubic [6, 7].

In the present work we have been interested in the possibility of the CaC_2 solubility of other ionic carbides. The present study has included Na_2C_2 , Li_2C_2 , and CeC_2 . CeC_2 is tetragonal ($a = 5.49 \text{ \AA}$, $c = 6.49 \text{ \AA}$) [3] and is isostructural with CaC_2 (I) [6, 8]. Both CeC_2 and CaC_2 have two molecules per unit cell. Li_2C_2 is primitive monoclinic but this is not well established [9]. Na_2C_2 has been studied via neutron diffraction by Atoji [10] and was found to be tetragonal.

The ionic radii of Ca^{2+} , Ce^{4+} , Li^+ and Na^+ are 0.99, 1.01, 0.60 and 0.95 Å respectively [15]. On the basis of size alone, it might be expected that CeC_2 and Na_2C_2 would show the most solubility in CaC_2 (I).

A determination of solubility has been made

via an X-ray parametric method. This method is fully described in the literature [11, 12] and will only briefly be reviewed here. In general it has been observed that a solute B will either increase or decrease the lattice parameters of a solvent A . If B is continuously soluble in A a plot of lattice parameter versus mole per cent often yields a straight line in ionic compounds. This result is known as Vegard's law [11]. Should a solubility limit of B in A occur, a discontinuity in the slope of the line will appear since the lattice parameters of the phase being formed will remain constant after the solubility of B in A has been exceeded. It was the purpose of this work to determine the change in the lattice parameters of CaC_2 (I) with respect to additions of CeC_2 , Na_2C_2 and Li_2C_2 .

2. Experimental procedure

The compounds used in these experiments were obtained in powder and lump form. Samples of mixed carbides were prepared by weighing out appropriate amounts of constituent chemicals in a glove box using P_2O_5 as a desiccant. All the compounds used in these experiments react with atmospheric water. After initial mixing, the carbides were sealed in a pre-dried plastic container and ball-milled for 15 to 20 h. This last procedure was to insure a random mix of the powders.

Small samples were pressed into a disc approximately 2.5 cm in diameter and 1 to 2 mm thick. Pressing pressure was 10 000 to 12 000 psi. The disc was transferred to an alumina crucible for

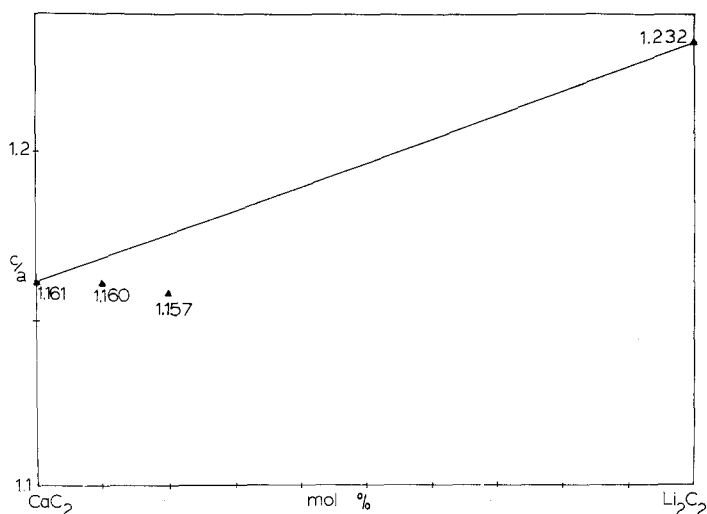


Figure 1 Lattice parameter ratio (c/a) of CaC_2 (I) versus mole per cent Li_2C_2 .

heat-treatment. The alumina crucible was fitted with a tantalum bottom and top because CaC_2 reacts with Al_2O_3 at 1250°C [13]. The discs were heat-treated in a vacuum furnace. The calcium-sodium carbide mixtures were either heated at 600°C for 5 h at 2 to 5 microns or at 500°C for 5 h under 50 mm argon. A comparison of results showed no significant difference between the two procedures.

Calcium carbide-lithium carbide and calcium carbide-cerium carbide mixtures were heated at 500 and 400°C respectively for 5 h at 2 to 5 microns.

After a heat-treatment was completed the disc was removed from the furnace and mounted in clear diallyl phthalate plastic. The final X-ray sample was a clear plastic disc with the disc of sample material embedded in the centre at one of

the end surfaces. $\text{CuK}\alpha$ radiation was used, and the lattice parameters were calculated from the d -spacings and Miller indices of each identifiable peak by computer analysis [14].

3. Results and discussion

Figs. 1 to 3 show the lattice parameter ratio c/a for CaC_2 as a function of the mole per cent of Li_2C_2 , Na_2C_2 , and CeC_2 added. As may be seen, sodium and lithium carbide show no solubility in calcium carbide (Figs. 1 and 2). The reported value of c/a for calcium carbide is 1.161 [3]. If lithium carbide had been soluble in calcium carbide the respective values of c/a at 10 and 20 mol % of lithium carbide in calcium carbide would have been approximately 1.168 and 1.172 if Vegard's law was obeyed. In the case of sodium carbide these values should have been 1.230 and 1.130.

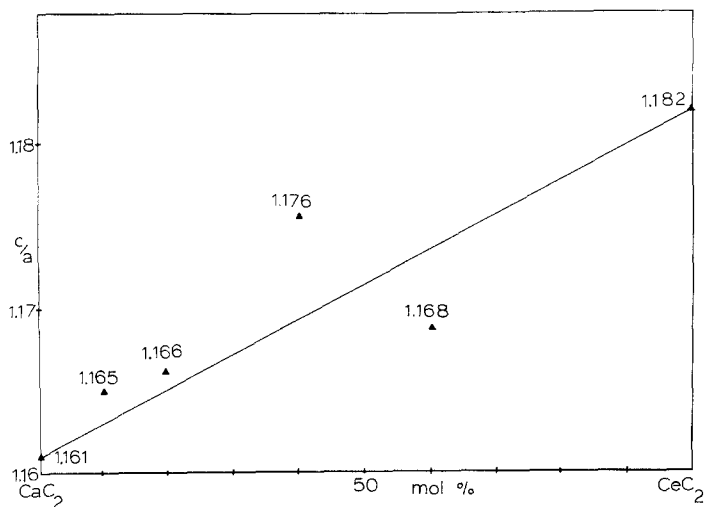


Figure 2 Lattice parameter ratio (c/a) of CaC_2 (I) versus mole per cent of Na_2C_2 .

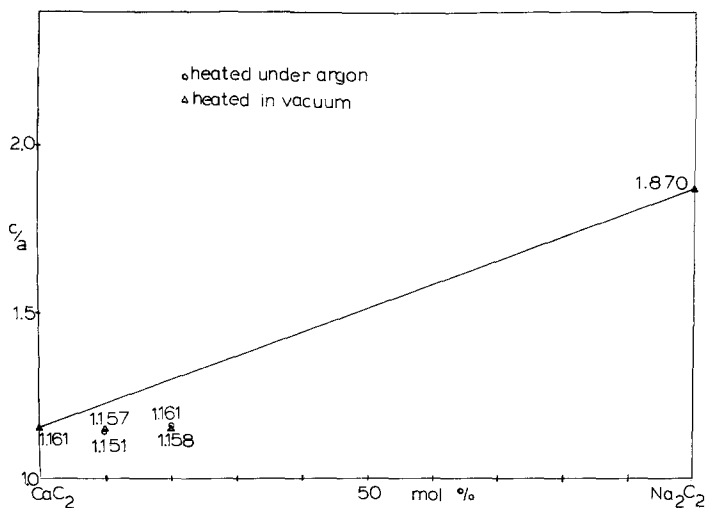


Figure 3 Lattice parameter ratio (c/a) of CaC_2 (I) versus mole per cent CeC_2 .

Solubility was found in the calcium carbide–cerium carbide system. Fig. 3 demonstrates this. Although there is significant error, the measured parameters appear to shift in accordance with Vegard's law, as shown by the indicated straight line from the CaC_2 (I) c/a ratio of 1.161 to the CeC_2 c/a ratio of 1.182. Table I gives the a and c parameters for each composition as well as c/a ratios. CeC_2 appears to be soluble up to at least 40 mol%. An attempt was made to make an 80 mol% CeC_2 in CaC_2 (I) sample, however at this concentration of CeC_2 the sample decomposed.

4. Conclusion

It has been found via X-ray parametric methods that CeC_2 is substantially soluble in CaC_2 (I) as might be expected since both have the same crystal structure. Neither Na_2C_2 nor Li_2C_2 appear to be significantly soluble in CaC_2 .

TABLE I Lattice parameters of the CaC_2 – CeC_2 mixtures

Composition mol% CeC_2	a (Å)	c (Å)	c/a
0	5.49	6.38	1.161
10	5.456	6.354	1.165
20	5.467	6.374	1.166
40	5.465	6.374	1.176
60	5.495	6.410	1.168
100	5.49	6.49	1.182

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