the liquid silicon phases. Published data (see Table 5.7) clearly show that the elements belonging to the Group IIIA (B, Al, Ga) and the Group VA (P, As, Sb) have a coefficient close to 1, making it difficult to separate them from the silicon. These elements are the electronic dopants for silicon and their concentration must be closely controlled during all steps of the manufacturing process. Their chemical and physical behaviour in interaction with silicon are two aspects of their close neighbourhood to this element. Crystallisation as such cannot be satisfactory without prior treatments, specifically to remove these elements, particularly P and B.

- *Crystallisation from a silicon-melt*: Various methods have been claimed to be useful for refining silicon by directional solidification resulting in large oriented crystals. All these various crystallisation methods are also used in manufacturing the silicon photovoltaic devices, and they are described in Chapter 6 of this handbook. Other valuable references are to be found in [39, 40].
- *Crystallisation from an aluminium melt*: Silicon forms a unique eutectic phase at the concentration of 12.6%(w) in aluminium. Several companies (Union Carbide, Alcoa and Wacker) have tried to take advantage of this property in order to purify silicon. By cooling a hypereutectic composition, pure silicon phases crystallise and precipitate from the aluminium melt. After solidification of the hypereutectic alloy, the aluminium matrix can be dissolved by leaching, releasing the pure silicon crystals [39, 41–44]. Published data indicated that the aluminium content in the resulting silicon was as high as 300 ppm(w). The segregation coefficient of aluminium in silicon limits further separation. A further reduction of aluminium, by directional solidification of the silicon thus obtained, would add unacceptable cost just for this element. Other metallurgical routes to eliminate Al at 1 ppm(w) level or less need to go through silicon melting and subsequent extraction with the double risk of recontamination and heavy material losses.

5.7.2 Upgrading Purity of the Metallurgical Silicon Route

The processes used in the elaboration of metallurgical grade silicon for the aluminium and the chemical industries proves that most of the metallic impurities could by repetition and combination of methods be decreased to a rather low level, for example 100 ppm(w) (see Table 5.9). Since metals could be further decreased by a post-directional solidification, it was rational to explore the full potential of this expected low-cost route.

5.7.2.1 Use of pure raw materials and pure lining

The use of pure linings in the furnaces and the intermediate vessels containing the liquid silicon was a first approach. It was investigated by several companies and research

Table 5.9 Typical best results achieved with the carbothermic reduction using high-purity raw materials

Impurity	B	P	Al	Fe	Ti
Minimum content ppm(w)	2	1	100	100	10
Maximum content ppm(w)	4	3	300	200	20