High-vacuum synthesis of SiC from rice husk: a novel method

2013 J. Phys. D: Appl. Phys. 46 345306

(http://iopscience.iop.org/0022-3727/46/34/345306)

IOP Publishing Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. **46** (2013) 345306 (6pp) doi:10.1088/0022-3727/46/34/345306

High-vacuum synthesis of SiC from rice husk: a novel method

M Sarangi[1], B Mallick[2], S C Mishra[3], T N Tiwari[4] and P Nayak[1]

[1] Department of Physics, Sambalpur University, Jyoti Vihar 768019, India
[2] Institute of Physics, Bhubaneswar 751005, India
[3] Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela 751008, India
[4] Unique Research Centre, Rourkela 769014, India

E-mail: bmallick@iopb.res.in

Received 14 May 2013, in final form 4 July 2013
Published 7 August 2013
Online at stacks.iop.org/JPhysD/46/345306

Abstract

A new technique for the production of SiC from rice husk is reported in this paper. The high-purity β-SiC is synthesized in a short time of 5 min. The samples are characterized by x-ray diffraction and scanning electron microscopy analysis. The results are compared with the previously reported result that was obtained by conventional process.

(Some figures may appear in colour only in the online journal)

1. Introduction

Silicon carbides are widely recognized as materials with high mechanical wear resistance, hardness and thermal and chemical stability within the set of modern ceramics [1, 2]. Silicon carbide (SiC) whiskers are a potential reinforcement for producing strong and tough ceramic and metal matrix composites. At present, most SiC whiskers are produced by the carbothermal reduction of silica. A number of methods are adopted using various sources of silica and carbon for the synthesis of SiC. An ultra-pure form of silicon carbide is synthesized from the pure form of the materials (single phase) by applying high-vacuum techniques such as: molecular-beam epitaxy (MBE), chemical vapour deposition (CVD), vacuum sublimation, ion-beam synthesis [3] and nonequilibrium hetroepitaxy [4, 5]. All the above methods fail to synthesize SiC from multi-phase materials like rice husk (RH). In the particular case of β-SiC, the processes to obtain fibres and particles are expensive; these consist conventionally of the use of CVD and vapour–liquid–solid (VLS) techniques in electrical furnaces [6]. SiC whiskers can be produced by the thermal decomposition of potentially inexpensive agricultural waste such as RH. RHs produce a high ash content, containing silica varying from 13 to 29 wt% depending on the variety, climate and geographic location.

India is one of the largest rice-producing countries in the world. Therefore, a large quantity of RH is generated as a by-product of rice milling and is considered to be an agricultural waste. It has been estimated that 54 million tons of RH is produced every year [1]. Burning has been the primary means of its disposal. Not only does the burning of RH create pollution problems, but the extremely fine silica ash is also toxic and thus constitutes a health hazard. Even careful incineration procedures cannot completely eliminate this airborne silica. Thus, the burning of RH with its attendant problems of air pollution and ash disposal has proven to be an unsatisfactory solution. Fortunately, RH contains both the necessary carbon and silica, in intimate contact, to provide a nearly ideal source material for the production of SiC, an industrially important ceramic material. RH was first used by Cutler (1973) as a starting material for the production of silicon carbide [7]. Since the RH route appears to be promising, much attention has been paid to it [8–18].

Almost all the processes investigated so far involve two process steps, viz. (i) coking at a lower temperature (400–800 °C) in a controlled manner to remove volatiles, and (ii) reacting the coked RH at a high temperature (>1300 °C) to synthesize SiC. Material synthesized in the above two-step process using a traditional atmosphere (N_2/Ar) furnace or low-vacuum furnace produces poor-quality SiC because of the presence of impurities in the form of the solid mixture or impurities present in gas (N_2/Ar). Since leakage at very high temperature is a common problem in these furnaces, it is technically difficult to synthesize high-purity SiC phases using traditional furnaces. In another work, Krishnarao *et al* showed that rapid heating is more favourable in the production of SiC [19]. So, in a novel approach, we have attempted to synthesize SiC from RH in a modified single step with rapid

Figure 1. The arrangement of the filament with the graphite crucible.

heating in a high vacuum, and this paper gives a detailed account of this work.

2. Experimental details

2.1. Sample collection and preparation

The RH was collected from a local rice mill with husk dimensions of 7–10 mm long, 1.5–2.0 mm wide and 0.10–0.15 mm thick. Dry raw RHs (RRHs) were washed thoroughly with water to remove the adhered soil and other contaminants present in them and then were dried in the sunlight for 24 h. These were designated as RRH. Acid leaching was performed by treating the RRH with dilute HCl (1 : 1) in distilled water for 1 h. It was then washed thoroughly with distilled water followed by treatment with a dilute ammonia solution (10 vol%) for 1 h to remove the traces of acid. The treated husk was taken out and washed thoroughly in distilled water followed by drying in air for 24 h. This is designated as acid-treated RH (ARH). ARH was heated in a furnace at 700 °C for 2 h in an N_2 atmosphere to preserve the carbon in the sample, and hence black ash (BA) was obtained.

2.2. Small graphite furnace

A graphite crucible, as shown in figure 1, was attached with the tungsten heating filaments at the conical bottom of the crucible. This small graphite oven consists of a small cylindrical graphite crucible (outer diameter 14 mm, internal diameter 12 mm and length 30 mm excluding the conical tip (10 mm)) covered by a cap with an axial hole (5 mm) as the outlet of the gas.

2.3. High-vacuum system

A high-vacuum coating unit (Hind HighVacuum, India), designed for the synthesis of thin films by the resistance heating technique, has been used. There is a provision for variable voltage (0–200 V) and current (0–100 A), independently, for the resistance heating. Like all other traditional vacuum-coating units, it consists of a view port, gas (inert) inlet pin valve port, air inlet port, cooling lines, etc. The ultimate vacuum of the system can be obtained at around 2×10^{-6} mbar with the help of the attached pumping system (a diffusion pump followed by a rotary pump).

2.4. Synthesis

As reported in a previous work [20], it is possible to synthesize phase-pure SiC from pure powders of silicon and carbon in a temperature range <980–1300 °C. Again, as reported in the earlier paper [21], the suitable temperature range for the formation of SiC from RH is 1100–1400 °C. Therefore, to carry out the heating experiment in the above range, crystalline silicon, whose melting point is about 1414 °C, was selected as a standard material for the temperature calibration. Another important aspect of the selection of Si crystal for heating in the graphite crucible before the treatment of the experimental sample (RH material) was to prepare a reference SiC material for comparison purposes.

The above high-vacuum coating unit was modified for the treatment of RH for the synthesis of SiC. For the standardization value of current and voltage, we kept the Si-crystal in a crucible made of graphite and introduced it into the heating zone of the furnace. A W-filament was used for heating purposes in the heater. The whole system was sealed and vacuumed up to 4.2×10^{-6} mbar. The vacuum system was locked, so that it could be held for a longer period. In this newly designed furnace, the temperature increases rapidly. It has been observed that after about 2 min, the volatiles are removed. The furnace was set to heat the sample up to 1414 °C in a shorter time, with 5 min soaking time in a high vacuum. Voltage and current were adjusted by observing the melting state of the Si in the high-vacuum system. Here, we found that the standardized value of voltage and current was 20 V and 80 A, respectively. But the time taken to reach the melting point of the Si crystal was very small compared to traditional methods, i.e. only 5 min. Finally, the sample was cooled down slowly for 24 h; after that the vacuum was broken by introducing ultra-pure nitrogen. No gas was introduced to cool down the system. Then, the treated silicon sample was taken out after breaking the vacuum. Similarly, for the experiment of our interest, BA was placed in the high-vacuum system and the standardized value of power (20 V, 80 A) was adjusted for the synthesis of SiC (soaking time 5 min). However, one can directly introduce the RRH in the small graphite crucible placed in the high vacuum. In that case, the power should be set at 20 V/30–40 A to burn the RRH during backing-roughing of the vacuum system. After that, the power should be gradually increased up to 20 V/80 A, when the system attains a high vacuum.

2.5. Characterization

A modified single step was adopted to prepare SiC directly from RRH in an indigenously developed experimental set-up using graphite crucibles. Figure 1 shows the schematic diagram of the set-up. A graphite crucible containing the BA was placed in the vacuum. The treated sample was found to be fragile in nature, thus it could be easily ground in a mortar and pestle. The sample was then characterized by x-ray diffraction (XRD) (Philips) for phase analysis and by a scanning electron microscopy (SEM) (JEOL).

3. Results and discussion

RH contains silica (in hydrated amorphous form) and cellulose, which yields carbon when thermally decomposed. When such a product is further heated at a high temperature (⩾1400 °C), a reaction occurs between the silica and carbon, resulting in the formation of SiC. The possible reactions in such a process can be written as follows:

$$\mathrm{C(s) + SiO_2(s) \rightarrow SiO(g) + CO(g)},$$

$$\mathrm{SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g)},$$

$$\mathrm{C(s) + CO_2(g) \rightarrow 2CO(g)},$$

$$\mathrm{2C(s) + SiO(g) \rightarrow SiC(s) + C(g)},$$

resulting in the overall reaction

$$\mathrm{SiO_2\ (amorphous) + 3C\ (amorphous) \rightarrow SiC + 2CO}.$$

3.1. XRD analysis

The XRD pattern of heat-treated BA obtained by applying this new technique is shown in figure 2(*a*). All of the strong reflection peaks are indexed, which shows that very high-purity and crystalline SiC phases are observed. However, it was noticed that, in the earlier method, an SiC peak was formed, along with many other phases such as cristobalite, Si_3N_4, Si_2N_2O, graphite and an intermediate phase Fe–Si [21]. In the present analysis, the characteristic reflection peaks (at $2\theta \approx 36^\circ$, 60° and 70°) of β-SiC (ICDD No 75–0254) have been assigned to the (1 1 1), (2 2 0), (3 1 1) planes. Only one peak shows the presence of unreacted silica (ICDD No 78–1252) in crystalline form at $2\theta \approx 26^\circ$. Silica in amorphous form is available naturally in RH. So, after heat treatment, the amorphous silica and carbon present in the sample react to form the SiC phases. As shown in table 1, the intensity of the SiC peak is much higher than in the earlier method [21]. This may be due to the reason that, at temperatures lower than that of SiC formation, the crystallization of silica was observed to be the dominant process. But due to rapid heating and the short holding time at pyrolysis temperatures, the formation of crystalline silica could be observed to be much less [20]. So, the percentage formation of SiC is enhanced.

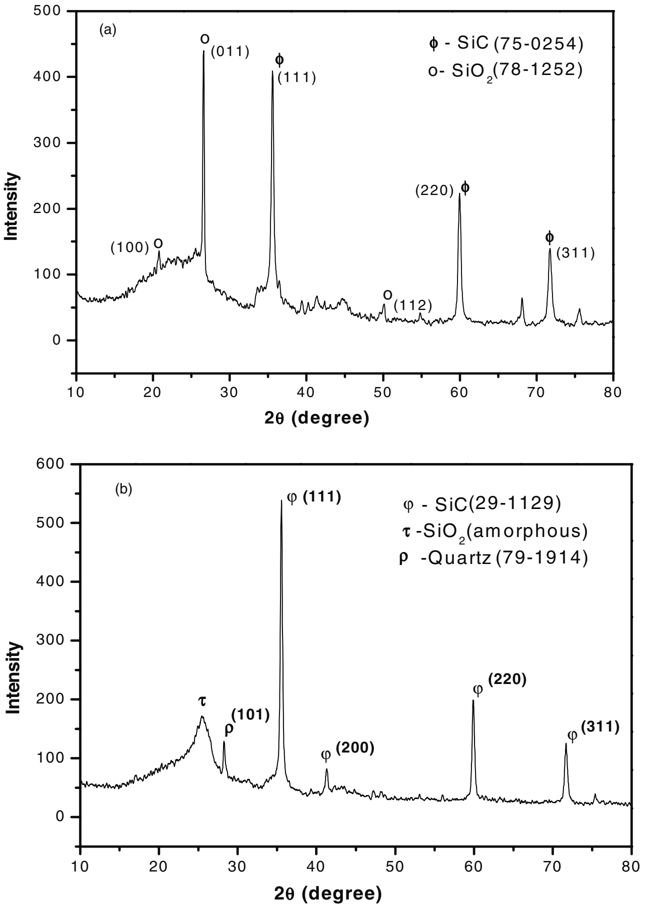

Figure 2. (*a*). XRD pattern of Fe-treated BA pyrolysed by the new technique at 1400 °C for 15 min. (*b*) XRD pattern of SiC phases formed during the heating of an Si crystal in a thin graphite crucible.

Figure 2(*b*) shows the XRD pattern of heat-treated silicon crystals (SC) in a thin graphite crucible. In this case, the SiC peaks (ICDD No 29–1129) are observed at $2\theta \approx 36^\circ$, 41°, 60° and 70° in the diffraction pattern and are presented in table 2. A small peak of silica can be observed at $2\theta \approx 28^\circ$. This silica might have formed during the seal-breaking process. Under exposure to oxygen, the surface of the silicon wafer gets oxidized to form silicon dioxide (SiO_2). The above silica on the surface of the wafer is quite stable and difficult to remove, even in a high vacuum. Again, on the surface, thermal oxidation of Si crystals might have taken place to form a small amount of silica. So, it is attributed that the SiC formation might have taken place by the reaction SiO_2 (amorphous) + 3C (amorphous) → SiC + 2CO. The major SiC peaks almost match the previous case (figure 2(*a*)). From both tables, it is observed that the full-width at half- maximum (FWHM) (ω) value of β-SiC phases synthesized from the RH is greater compared to the SC, i.e. $\omega_{\mathrm{RH}} > \omega_{\mathrm{SC}}$. This indicates that the crystallite size of the SiC formed from the RH is smaller compared to the crystallite formed from the SC.

The most intense peak observed (figure 2(*b*)) at $2\theta \approx 35.6^\circ$ is assigned as that of the β-SiC (1 1 1) phase. Comparing both results, it has been found that $I_{111}(\mathrm{SC}) > I_{111}(\mathrm{RH})$, which indicates that the formation of the β-SiC (1 1 1) phase from the silicon crystal is larger compared to that

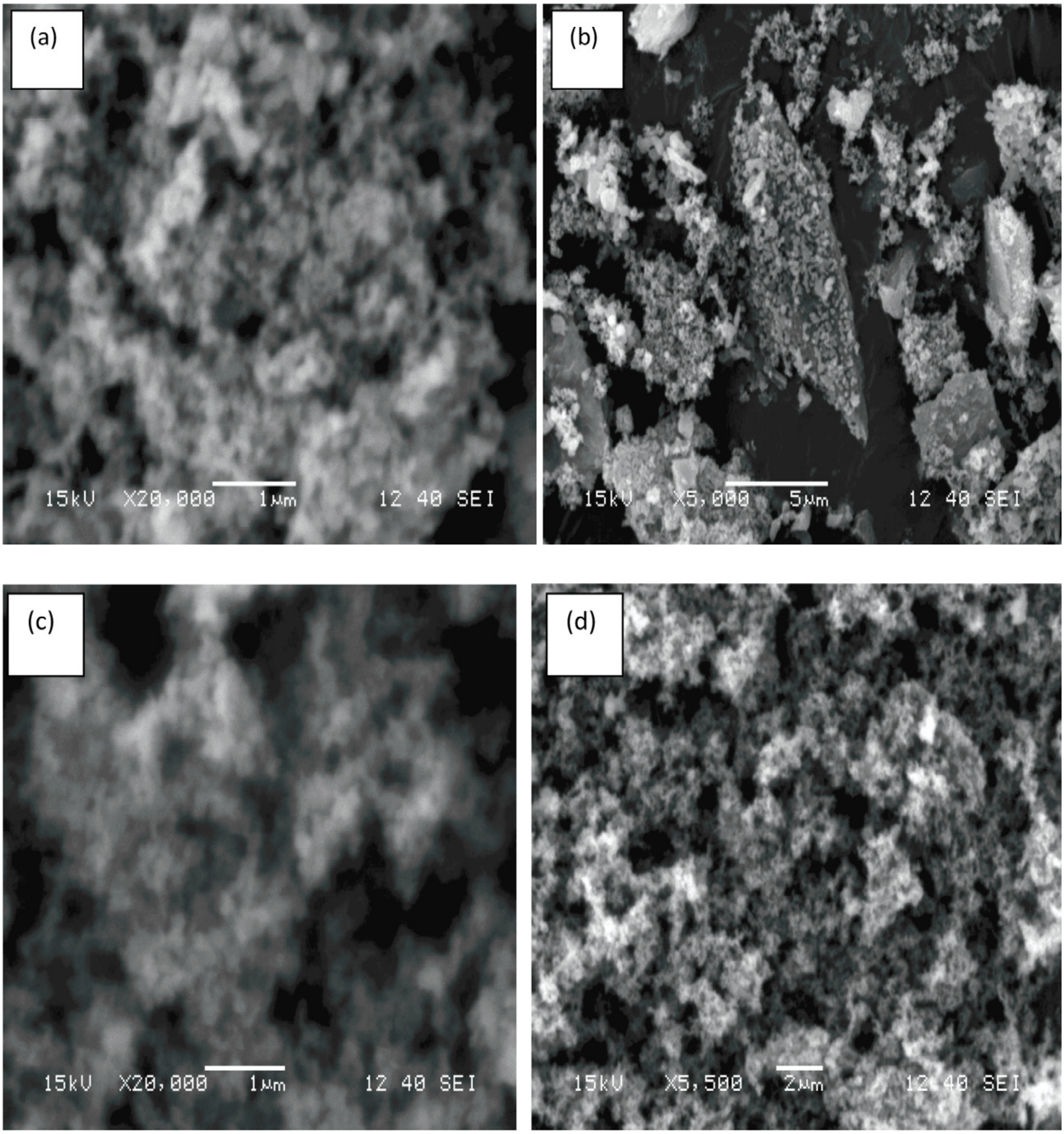

Figure 3. (*a*) and (*b*). SEM micrograph of SiC synthesized from RH with different magnifications. (*c*) and (*d*): SEM micrograph of SiC synthesized from a silicon crystal applying the high-vacuum synthesis technique.

from the RH under the same experimental conditions. Again, I_{220}(RH) > I_{220}(SC), which indicates that the β-SiC (2 2 0) phase crystallinity is more in the case of the RH with respect to the SC. Again, the amorphous hump observed at around 26° shows the presence of silica. This amorphization might have taken place due to the heating of the silicon crystal.

3.2. SEM analysis

An SEM micrograph of the sample pyrolysed by the new technique is shown in figures 3(*a*)–(*d*). Very small particles were observed to be formed after pyrolysis. Some charred particles are observed to be white in colour, which may be due to the formation of crystalline silica. The grey particles were observed to be SiC as also confirmed from the energy-dispersive spectroscopy (EDS) analysis. A large number of grey particles of approximately submicron size can be observed, showing the formation of SiC. The grain sizes of the particles, found from the scale, were approximately 100–200 nm. The charred particles obtained from RH (figures 3(*a*) and (*b*)) were fibrous, agglomerated and smaller, showing that the reactions had mainly taken place in the vapour–liquid

Table 1. Phase analysis data on Fe-treated BA pyrolysed at 1400 °C for 15 min.

Pos. (°2θ)	Height (cts)	FWHM (°2θ)	d-spacing (Å)	Rel. Int. (%)
20.7493	25.61	0.2362	4.280 99	6.53
26.6186	392.27	0.1378	3.348 88	100.00
35.6015	356.28	0.2755	2.521 81	90.83
39.4279	14.60	0.2362	2.285 44	3.72
41.3299	18.62	0.4723	2.184 56	4.75
44.8958	18.47	0.9446	2.018 99	4.71
50.1438	26.61	0.2755	1.819 30	6.78
54.9037	9.49	0.9446	1.672 30	2.42
59.9221	194.52	0.3542	1.543 69	49.59
68.0752	50.79	0.1574	1.377 32	12.95
71.7295	116.19	0.3936	1.315 88	29.62
75.6013	26.00	0.3840	1.256 78	6.63

Table 2. XRD pattern of SiC phases formed during heating of the Si crystal in a graphite furnace.

Pos. (°2θ)	Height (cts)	FWHM (°2θ)	d-spacing (Å)	Rel. Int. (%)
28.2455	63.47	0.1574	3.159 57	11.74
35.5744	540.65	0.1968	2.523 67	100.00
41.3141	41.72	0.2362	2.185 36	7.72
59.8592	176.18	0.3149	1.545 16	32.59
71.6945	112.81	0.2755	1.316 43	20.87
75.4471	12.39	0.5760	1.258 96	2.29

state. In the case of the Si crystal, particles seemed to be a little larger (figures 3(*c*) and (*d*)) and more uniform. This can also be observed from the XRD analysis. From tables 1 and 2, it can be seen that the FWHM value of the SiC phase (where $2\theta \approx 35.5°$) is larger in table 1 (i.e. in the case of RH) than in table 2 (i.e. in the case of the Si crystal). So, the crystallite size is smaller in case of RH than in the Si crystal.

In case of RH, more whiskers or fibrous (figure 3(*a*)) structures can be observed. In RH, very small amounts of metallic impurities (like Fe) could be observed to exist in the liquid state; hence the formation of whiskers might have taken place [21]. In case of particles obtained from an Si crystal, no impurities were present. Hence, formation of fibrous structures couldn't be observed (figure 3(*c*)).

3.3. EDS analysis

EDS analysis of the sample (figure 4) also confirms the presence of Si, C and O. The weight % of Si was found to be very less in the sample obtained from the Si crystal than in the RH (figure 4). Silicon and carbon usually react at a very high temperature, and a relatively low temperature was applied here for the purpose. The SiC formation might have taken place during the breaking of the vacuum. Because during that time some oxygen may react with the Si and C to form SiO and CO, hence it reacts to form SiC [21].

The whole reaction seems to be formed only on the surface of the Si wafer. So, the amount of Si present in EDS analysis can be observed to be thus less (tables 3 and 4). The wt% of carbon is much higher in the case of RH than in the Si crystal. In RH, the sample BA itself contains a large amount of amorphous carbon. But in the case of the Si crystal, only pure Si wafer was used. In both the cases, some amount of carbon was added from the graphite container in the form of graphite. So, the carbon content was less in the Si crystal than in the RH.

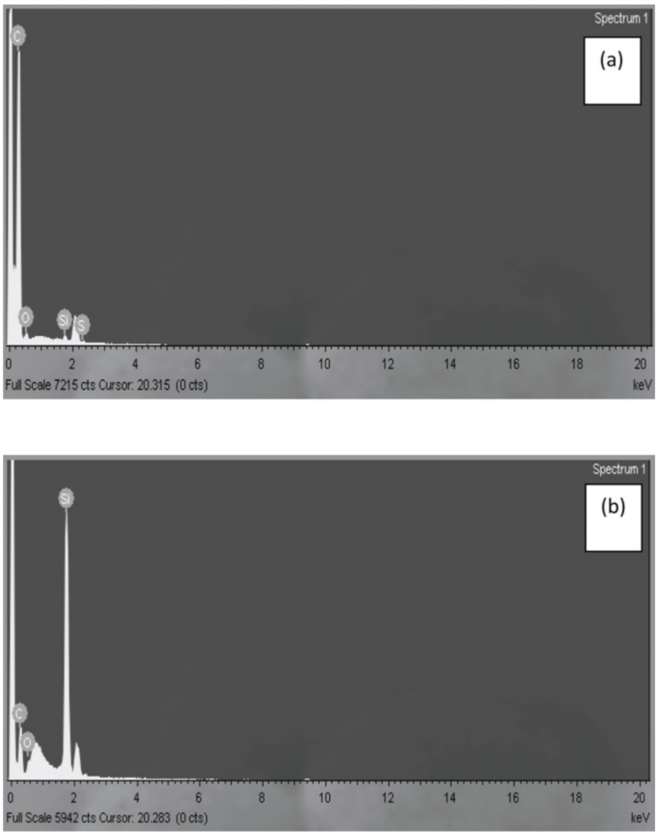

Figure 4. EDS analysis of pyrolysed RH (*a*) and silicon crystal (*b*) in a graphite crucible obtained by applying a high-vacuum technique.

Table 3. EDS data of various elements obtained from RH.

Element	Appr. Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	102.27	1.6618	88.99	1.08	92.07
O K	2.87	0.4493	9.25	1.08	7.19
Si K	0.76	1.0164	1.08	0.13	0.48
S K	0.46	0.9703	0.68	0.13	0.26
Total			100.00		

Table 4. EDS data of various elements obtained from the Si crystal.

Element	Appr. Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	11.49	0.3700	57.95	1.19	74.38
O K	1.76	0.5344	6.14	1.09	5.92
Si K	21.02	1.0922	35.90	0.96	19.71
Total			100.00		

4. Conclusion

In the present synthesis process, high crystalline β-SiC particles of very fine size were formed along with some amount of unreacted silica. So, the new technique has been found to be more beneficial towards the production of SiC from rice husk than the conventional process. We can conclude from the above experimental design of a high-vacuum mini graphite furnace that this can be very applicable in synthesizing various types of materials and, alternatively, metallurgical modification. It has lots of advantages over commercial furnaces or plasma reactors, which are: (i) the variable heating value and time required for synthesis is less; (ii) no continuous flow of argon gas is required; (iii) high-purity SiC can be synthesized; (iv) the formation of toxic pollutants like silica ash can be absorbed by the oil filter; and (v) compared to a plasma reactor, it is less expensive. So, this can be very useful in the development and preparation of various types of material in the future, especially in the area of material science.

However the main limitation of the above technique is the damage of the high-vacuum components due to the emission of volatile materials during heating in a single step. Necessary precautions and modifications of the vacuum unit are required. This requires an oil filter to be mounted on the exert port of the rotary pump to absorb the toxic pollutants emitted during heating.

References

[1] Martinez V, Valencia M F, Cruz J, Mejia J M and Chejne F 2006 *Ceram Int.* **32** 891

[2] Chen J, Qian W, Ye Y and Chen Q 2006 *J. Phys. D: Appl. Phys.* **39** 1472

[3] Katharria Y S, Kumar S, Singh F, Pivin J C and Kanjilal D 2006 *J. Phys. D: Appl. Phys.* **39** 3969

[4] Kukushkin S A, Osipov A V, Gordeev S K and Korchagina S B 2005 *Tech. Phys. Lett.* **31** 859

[5] Kukushkin S A and Osipov A V 2013 *J. Appl. Phys.* **113** 024909

[6] Milewski J V, Gac F D, Petrovic J J and Skaggs S R 1985 *J. Mater. Sci.* **20** 1160–6

[7] Cutler I B 1973 *US Patent* 3754079

[8] Manosur N A L and Hanna S B 1979 *Trans. J. Br. Ceram. Soc.* **78** 132

[9] Nutt S R 1988 *J. Am. Ceram. Soc.* **71** 149

[10] Patel M 1991 *Silicon Ind.* **55** 30

[11] Ray A K, Mohanty G and Ghose A 1991 *J. Mater. Sci. Lett.* **10** 277

[12] Singh S K, Stachowicz L, Girshick S L and Pfender E 1993 *J. Mater. Sci. Lett.* **12** 659

[13] Romera F J N and Reinso F R 1996 *J. Mater. Sci.* **31** 779

[14] Moustafa S F, Morsi M B and El-Din A A 1997 *Can. Metall. Q.* **36** 355

[15] Krishnarao R V, Mahajan Y R and Kumar T J 1998 *J. Euro. Ceram. Soc.* **18** 147

[16] Padmaja G and Mukunda P G 1999 *J. Am. Ceram. Soc.* **82** 1393

[17] Janghorban K and Tazesh H R 1999 *Ceram. Int.* **25** 7

[18] Panigrahi B B, Roy G G and Godkhindi M M 2001 *Br. Ceram. Trans.* **100** 29

[19] Krishnarao R V and Subrahmanyam J 1996 *Ceram. Int.* **22** 489

[20] Satapathy L N, Ramesh P D, Agrawal D and Roy R 2005 *Mater. Res. Bull.* **40** 1871

[21] Sarangi M 2009 *Silicon* **1** 103