The Synthesis of Silicon Carbide in Rhombohedral Form with Different Chemicals

CrossMark

İ. AFŞIN KARİPER

This study describes the attempt at producing silicon carbide using a simpler and less costly method. Within the study, XRD, EDX, and FTIR analyses were performed to determine the structural properties of the product, and SEM analyses were used to identify its surface properties. The characteristics such as porosity and surface area were determined through BET analysis. The starting reagents were compared with the product using FTIR analysis, whereas the product was compared with a sample of SiC procured from a supplier who manufactures high-purity products through BET analysis. In EDX analysis, approximately 72 pct Si and 28 pct C were identified. The vibrational peaks of the synthesized product (characteristics Si-C bonds) were observed at around 1076 cm^{-1} (FTIR analysis). At the same time, the outcomes were compared with major publications in the literature.

I. INTRODUCTION

SILICON carbide (SiC) is an indispensable material for the industry in view of its hardness, low thermal expansion coefficient, and high thermal conductivity as well as its resistance against corrosion. At the same time, since it is a very durable semiconductor, it is also quite useful in the world of electronics.[1–3] In its structure, each Si or C atom is surrounded by 4 Si or C atoms. A strong sp^3 hybridization in tetrahedral form is observed among them. The distance between Si and C atoms is around 3.08 Å. These structural parameters give the above-mentioned features to SiC. It may be more illuminating to summarize typical features of silicon carbide in a table as shown in Table I.

In Table I, some values are given as an approximation or an interval. This is because of 250 different forms of silicon carbide, known at the moment. Especially, Zinc blende (cubic), 4H-SiC: Wurtzite (Hexagonal), 6H-SiC: Wurtzite (Hexagonal), and 15R-SiC: Rhombohedral structures are the most common ones. The extended version of this table can be obtained from the literature.

Until now, researchers have tried many methods for the synthesis and production of this valuable chemical; Acheson process is at the top of them.[7] This method, which is being used for years, is a carbothermic reduction method using SiO_2 as the starting material. The production can be performed at very high temperatures, such as 2473 K to 2673 K (2200 °C to 2400 °C).

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \qquad [1]$$
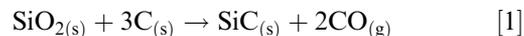
Using this method, α-SiC with very big particle size could be produced at high temperatures, which in fact makes the process costly. Some methods mentioned in the literature are outlined in Table II:

Here, researchers often used the elements such as Fe, Al, and Cu or their salts as catalyst. In fact, the catalyst should not react;, however, EDX analysis revealed that many researchers have detected catalyst contamination in the media if they failed to completely separate the product from the catalyst.[9–12] At the same time, SiO_2 contamination that has been observed in other methods is due to the oxidation of silica that naturally occurs when the heating process starts without making the media sufficiently inert. Of course, these contaminations were avoided in the studies conducted with high sensitivity. The costs of some of these methods are quite high because of the device required for the production or because of the necessity of very high temperatures. The productivity of the methods with low cost is not satisfactory. Even though products with low contamination can be produced with high efficiency through chemical vapor deposition and arc discharge methods, the cost of the devices and the experts who will use this equipment must also be taken into account.

At the moment, there are additional reviews and books in the literature. We tried to give brief information about SiC and reviewed some major studies performed for the production and synthesis of SiC. In this study, we attempted to find a simple and a low-cost method for the production of SiC. We compared the outcomes that we were able to measure within our facilities with the literature.

İ. AFŞIN KARİPER is with the Department of Science Education, Faculty of Education, Erciyes University, 38039, Kayseri, Turkey. Contact e-mail: akariper@gmail.com

II. EXPERIMENTAL

Solid powder high-purity Si, chloroform, acetonitrile and sodium metaborate were procured (Sigma Aldrich).

No purification was done to these chemicals. For the production of poly(hydrocarbyne): 10 mL chloroform was dissolved in 30 mL acetonitrile, whereas 1 g sodium metaborate was dissolved in 10 mL water. Dissolved sodium metaborate was added to chloroform-acetonitrile mixture. Electrolysis was performed with a current of 0.25 amps, 10 V, for a period of 1 hour. The obtained poly(hydrocarbyne) was filtered, and then boiled in the

condenser for 8 hours with LiAlH$_4$. It was filtered again, and washed with the solvents such as chloroform, THF. After getting dried completely, the solid was grinded with pure Si at 1:1 mol ratio [0.28 g Si and 0.13 g poly(hydrocarbyne)]. The mixture was oven-dried at 1273 K (1000 °C), in argon atmosphere for 48 hours, as shown in Figure 1.

The structural properties of SiC were measured by X-ray diffraction (XRD) with a CuKα_1 radiation source (Rikagu RadB model, $\lambda = 1.5406$ Å) over the range of 10 deg $< 2\theta <$ 90 deg at a speed of 3 deg min^{-1} with a step size of 0.02 deg. The surface properties of the films were examined using an EVO40-LEO computer-controlled digital scanning electron microscope (SEM). Quantitative elemental analysis was performed using an EDX spectrometer attached to SEM. Infrared spectrum of silica xerogel was recorded on a Perkin Elmer Spectrum 400 spectrometer with a resolution of 4 cm^{-1} using DTGS detector and 10 scans for each spectrum. The hardness of the materials was measured using DuraScan EmcoTest device. A load in the range from 50 to 100 g was applied on each material by a

Table I. Typical Features of SiC[4–6]

Crystal Structures	3C-SiC: Zinc blende (cubic)
	4H-SiC: Wurtzite (Hexagonal)
	6H-SiC: Wurtzite (Hexagonal)
	15R-SiC: Rhombohedral
Thermal Expansion Coefficient	2.77 (42) $\times 10^{-6}$ K^{-1}
Melting Point	3103 K (2830 °C) at 35 atm
Density	3.166 to 3.211 g/cm^3 at 300 K (27 °C)
Hardness	9.2 to 9.3 on the Mohrs scale
Refractive Index $n(D)$	2.55
Electron Mobility	~900 cm^{2}N.s

Table II. Common Methods for Producing SiC[8]

Methods	Reagent	Temperature	Potential Contaminations
Carbon-Nanotube Confined Reaction	SiO$_2$-C	1673 K (1400 °C)	SiO$_2$
Arc Discharge	SiO$_2$-C	3273 K (3000 °C)	SiO$_2$ catalyst
Laser Ablation	SiO$_2$-C	1173 K (900 °C)	SiO$_2$ catalyst
Sol–gel and Carbothermic reduction	SiO$_2$-C	1173 K to 1923 K (900 °C to 1650 °C)	SiO$_2$
Chemical Vapor Deposition	SiH$_4$-SiCl$_4$-Si(CH$_3$)Cl-CH$_3$SiCl$_3$,CH$_4$	1373 K (1100 °C)	Al-Cu
High-Frequency Induction Heating	SiO$_2$-C	1723 K (1450 °C)	SiO$_2$

- Synthesis of poly(hydrocarbyne)
  - Chloroform dissolved in acetonitrile was mixed with NaCl dissolved in a certain amount of water; then electrolysed with a voltage of 10 volts, for 1 hour. It was boiled with LiAlH4 and THF in a condenser for 8 hours and washed with many organic solvents, such as hexane, and dried.

- Synthesis of SiC
  - After getting dried, the solid was grinded with pure Si at 1: and poly(hydrocarbyne). The mixture was oven-dried at 1273 K (1000 ºC), in argon atmosphere for 48 hours.

Fig. 1—Synthesis progress of SiC.

diamond bit, and then the device calculated the hardness by regarding the surface of the trace left by the load and the force that it applied. Surface areas were examined through BET analysis. The porosity of the xerogels was calculated from Nitrogen adsorption–desorption isotherms of silica xerogels calcined at 523 K (250 °C).
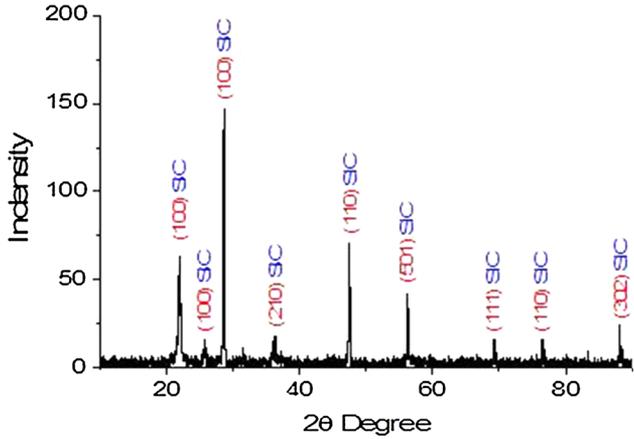
Fig. 2—XRD pattern of solid SiC.

III. RESULT AND DISCUSSION

The synthesis mechanism of poly(hydrocarbyne) and silicon carbide was modeled as below: [Eqs. 2 and 3].

$$CHCl_3 \longrightarrow \left[\begin{array}{c} H \\ | \\ C \\ \diagup | \diagdown \end{array} \right]_n + Cl_{2(g)} \qquad [2]$$

$$Si \quad + \quad \left[\begin{array}{c} H \\ | \\ C \\ \diagup | \diagdown \end{array} \right]_n \longrightarrow SiC_{(s)} + H_{2(g)} \qquad [3]$$
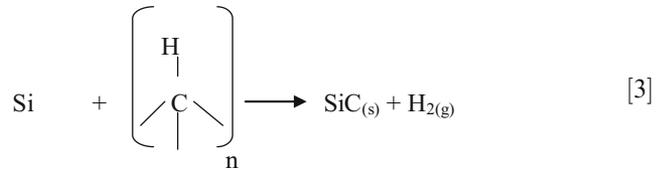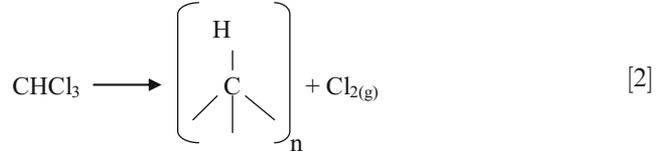
Equity (2) is the short representation of a very well-known pericyclic mechanism that works through electrolysis. Whereas equity (3) is a displacement mechanism, where both solid–solid diffusion and Si and proton play key roles at high temperatures. The yield of the reaction is approximately 90 pct.

The XRD pattern of a solid SiC is given in Figure 2. Solid SiC, form of which was identified as rhombohedral, completely matches with ASTM data files 73-2085

(a)

(b)

(c)
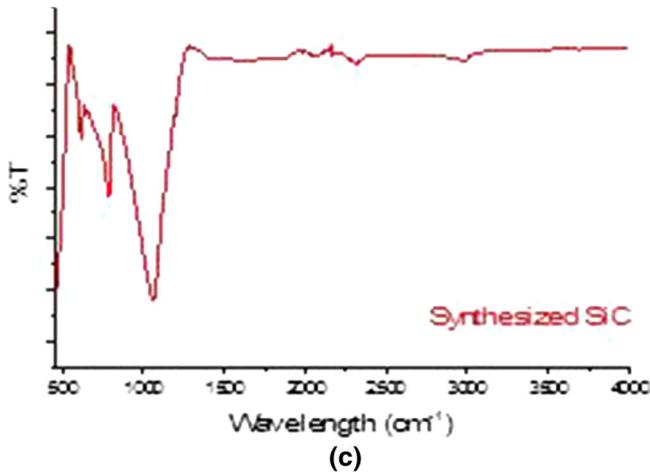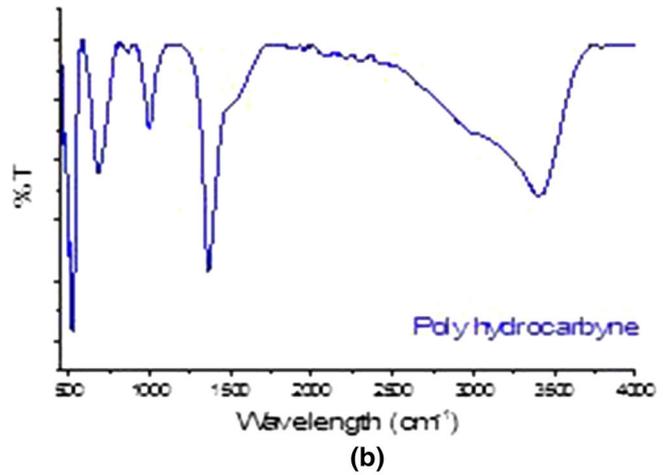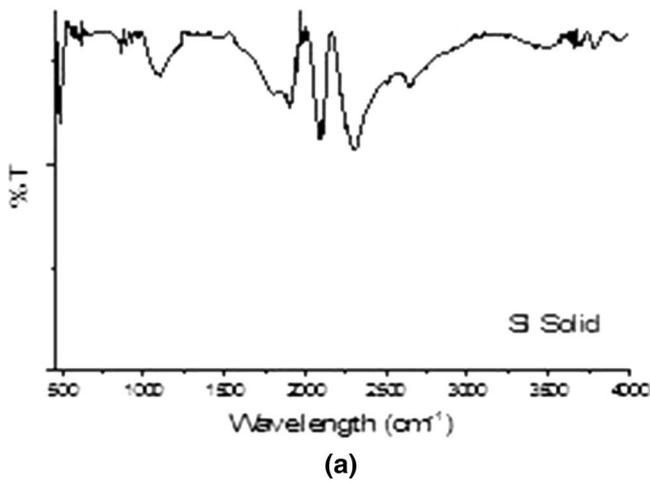
Fig. 3—FTIR spectra of (a) solid Si, (b) poly(hydrocarbyne), and (c) synthesized SiC.

and 73-2064. Cell parameters were $a = b$:3.06, c:188.12; SG:R3m. The strongest peak was observed at 28.549 deg, (100) direction. Yigezu *et al.* have also observed this peak.[13] Treffer *et al.*[14] have identified the strongest peak of SiC that they have synthesized to appear at around 53 deg, whereas Moshtaghioun *et al.*[15] have detected it at around 36 deg. However, the products of these researchers are the compounds in the form of β-SiC or α-SiC, and they are usually in hexagonal and cubic cell forms. The most important point here is that Si peak was observed at around 30 deg, and no pollution peak was observed.

Figure 3 displays FTIR analyses of solid Si that has been purchased as raw material (no additional purification was applied) (Figure 2(a)), poly(hydrocarbyne) that has been used in the synthesis (Figure 2(b)), and the solid SiC that we synthesized (Figure 2(c)). In Figure 2(a), the characteristic peaks of silica were observed at 2300 and 2084 cm^{-1}. In Figure 2(b), aliphatic −CH peaks combined with −OH peaks were observed at 3400 cm^{-1}. Signals of C-C tension were detected at 1366 cm^{-1}, C-H vibration was observed at 980 cm^{-1}, and again the peaks of C-H and C-C vibrations' signals were detected at 674 and 524 cm^{-1}. As mentioned in the literature, vibrational peaks belonging to C-O or C=C bonds were not observed.[16,17] In Figure 2(c), tension vibrations specific to SiC were observed at 776 cm^{-1}, whereas ω_{4LO} phonon peak was detected at 1075 cm^{-1} and ω_{1LO} phonon peak was detected at 601 cm^{-1}. Bianconi *et al.*[18] have observed characteristic SiC peak at 780 cm^{-1}, whereas in the detailed IR study performed by Karbovnyk *et al.*,[19] they have presumed to have seen ω_{4LO} phonon peak at 1082 cm^{-1}, and ω_{1LO} phonon peak at 596 cm^{-1}.

Figure 4 shows BET analyses and hardness values of the procured SiC and the one that we have synthesized. Surface area of the synthesized SiC was 1.64 m^2/g, whereas the surface area of the procured SiC, which has been used as the reference, was measured as 7.65 m^2/g. Regarding their hardness values, it has been found that the hardness of reference SiC was 11 GPa, whereas that of the synthesized SiC was 13 GPa; thus the synthesized
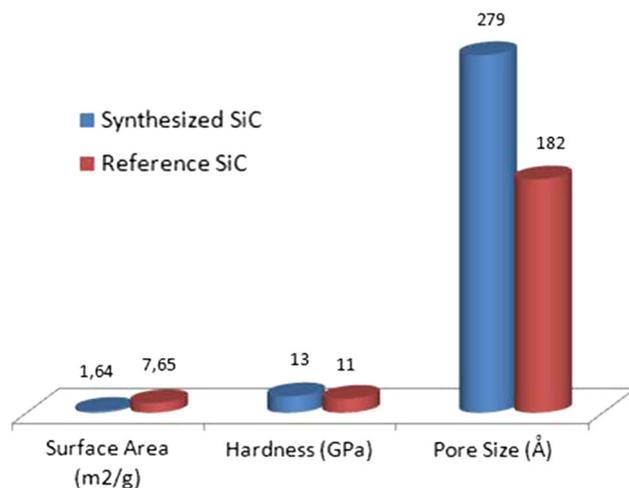
solid SiC was harder of the two. The pore size of the synthesized SiC was found to be 182 *vs* 276 Å. Munro[20] has produced α-SiC compound at 2773 K (2500 °C) and sintered at 1273 K (1000 °C) and measured the hardness of the compound to be around 10 GPa, using Vickers indentation method that we also used. This result is in line with the hardness of SiC that we have procured; however, it is lower than the hardness of SiC that we have synthesized. The surface area of the SiC that we have synthesized is quite low compared with the procured one, as well as the ones in the literature. Moene *et al.*[21] have measured the surface area of the SiC that they have produced using chemical vapor deposition as 25 to 68 m^2/g under 0.1 kPa N$_2$ pressure. The surface area of the SiC that Krawiec and Kaskel have produced[22] using CVD method was improved to 200 m^2/g; however, they have reported that the surface area of SiC produced commercially (as ours) is usually lower than 20 m^2/g. However, the techniques used by these researchers are based on crystal growing rather than solid powder production; thus, they should be evaluated as another category. At the same time, regarding XRD data of these studies, it should be noted that they were not crystalized as well as the SiC that we synthesized and XRD peaks can hardly be identified from the amorphous structure. Since a well-crystallized structure stacks more tightly, its surface area may be lower than amorphous or semiamorphous materials. It should be noted that the pore size of the SiC that we have synthesized is bigger than commercial high-purity SiC. Shiflett and Foley[23] reported that the pore sizes of
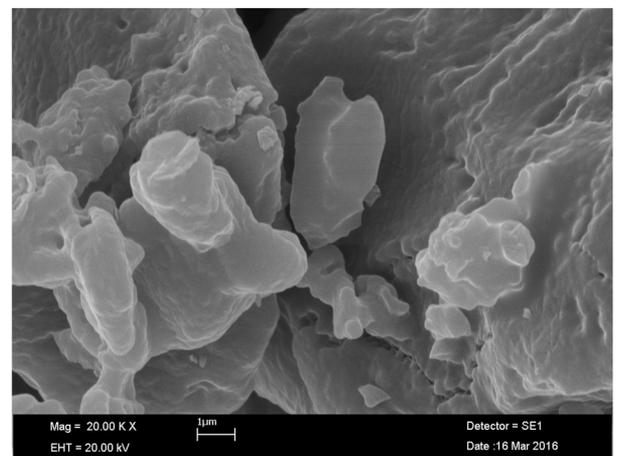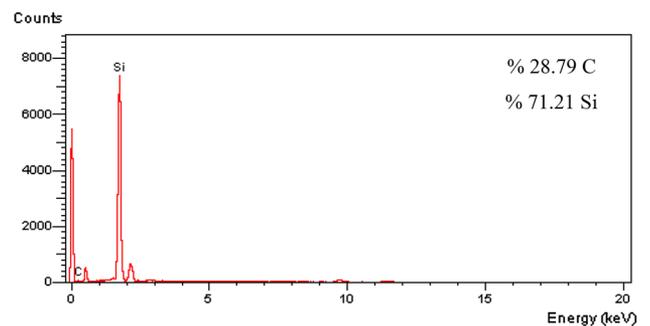
Fig. 5—SEM image and EDX analyses of synthesized SiC.

Fig. 4—Comparison of physicochemical properties of the synthesized SiC and reference sample.

the SiC produced until now usually range from 0.3 to 0.7 nm. According to these values, the pore size of the SiC that we have synthesized is quite high.

Figure 5 shows SEM image and EDX analysis of the synthesized SiC. The elemental ratio of C and Si, added during the synthesis (1:1) is found to be 28.79 pct C and 71.21 pct Si, whereas their empirical formula is $Si_{2.535}C_{2.399}$, which approximately corresponds to the SiC molecule. SEM image clearly shows the granular growth structure of SiC crystals.

IV. CONCLUSION

In this study, we attempted to improve the already known SiC production methods and also find a different method with lower cost, occurring at lower temperatures and which does not require any technical equipment for the production. We showed that SiC can be produced by pulling off the proton of C atoms in the poly(hydrocarbine) and attacking Si atoms with carbanion. We did not observe SiO_2, C=C, and C=O or C-O contamination through XRD and FTIR analyses. EDX analysis did not reveal the presence of any other element. Surface area was found to be lower than that of the procured commercial SiC and the SiCs synthesized in the literature; however, pore size and hardness, which are the two most important characteristics of this compound, were found to be higher.

ACKNOWLEDGMENT

REFERENCES

1. Y. Yang, Z.M. Lin, and J.T. Li: *J. Eur. Ceram. Soc.*, 2009, vol. 9, pp. 175–80.
2. B. Elyassi, T.W. Kim, and M. Sahimi: *Mater. Chem. Phys.*, 2009, vol. 118, pp. 259–63.
3. H.B. Jin, J.T. Li, M.S. Cao, and S. Agathopoulos: *Powder Technol.*, 2009, vol. 196, pp. 229–32.
4. Yu. Goldberg, M.E. Levinshtein, and S.L. Rumyantsev: in *Properties of advanced semiconductor materials GaN, AlN, SiC, BN, SiC, SiGe*, M.E. Levinshtein, S.L. Rumyantsev, and M.S. Shur, eds., Wiley, New York, 2001, pp. 93–148.
5. S.E. Saddow: *Silicon carbide biotechnology a biocompatible semiconductor for advanced biomedical devices and applications*, 1st ed., Elsevier, Waltham, 2012, pp. 122–24.
6. A.S. Gusev, S.M. Ryndya, A.V. Zenkevich, N.I. Kargin, D.V. Averyanov, and M.M. Grekov: *Mod. Electron. Mater.*, 2015, vol. 1, pp. 120–25.
7. X. Luo, W. Ma, Y. Zhou, D. Liu, B. Yang, and Y. Dai: *Nano. Scale. Res. Lett.*, 2010, vol. 5, pp. 252–56.
8. W.M. Zhou, Y.F. Zhang, X.M. Niu and Min G.Q: Lecture Notes in Nanoscale Science and Technology, 3, Springer, New York, 2008, p. 17.
9. H.J. Chio, H.K. Seong, J.C. Lee, and Y.M. Sung: *J. Cryst. Growth*, 2004, vol. 269, pp. 472–78.
10. G.W. Ho, S.W. Wong, D.J. Kang, and M.E. Welland: *Nanotechnology*, 2004, vol. 15, pp. 996–99.
11. HJ Li, ZJ Li, AL Meng, KZ Li, XN Zhang, and YP Xu: *J. Alloys Compd.*, 2003, vol. 352, pp. 279–82.
12. Y.J. Zhang, N.L. Wang, R.R. He, X.H. Chen, and J. Zhu: *Solid State Commun.*, 2001, vol. 118, pp. 595–98.
13. B.S. Yigezu, M.M. Mahapatra, and P.K. Jha: *J. Miner. Mater. Charact. Eng.*, 2013, vol. 1, pp. 124–30.
14. G. Treffer, J. Neuhiiuser, and G. Marx: *Mikrochim. Acta*, 1997, vol. 125, pp. 325–30.
15. B.M. Moshtaghioun, R. Poyato, F.L. Cumbrera, S. de Bernardi-Martin, A. Monshi, M.H. Abbasi, F. Karimzadeh, and A. Dominguez-Rodriguez: *J. Eur. Ceram. Soc.*, 2012, vol. 32, pp. 1787–94.
16. J. Hong, A. Goullet, and G. Turban: *Thin Solid Films*, 2000, vol. 364, pp. 144–49.
17. Y. Nur, H.M. Cengiz, M.W. Pitcher, and L.K. Toppare: *J. Mater. Sci.*, 2009, vol. 44, pp. 2774–79.
18. P.A. Bianconi, S.J. Joray, B.L. Aldrich, J. Sumranjit, D.J. Duffy, D.P. Long, J.L. Lazorcik, L. Raboin, J.K. Kearns, S.L. Smulligan, and J.M. Babyak: *J. Am. Chem. Soc.*, 2004, vol. 126, pp. 3191–202.
19. I. Karbovnyk, P. Savchyn, A. Huczko, M.C. Guidi, C. Mirri, and A.I. Popov: *Mater. Sci. Forum*, 2015, vols. 821–823, pp. 261–64.
20. R.G. Munro: *J. Phys. Chem. Ref. Data*, 1997, vol. 26, pp. 1195–1203.
21. R. Moene, L.F. Kramer, J. Schoonman, M. Makkee, and J.A. Maulijn: *Appl. Catal. A*, 1997, vol. 162, pp. 181–91.
22. P. Krawiec and S. Kaskel: *J. Solid State Chem.*, 2006, vol. 179, pp. 2281–89.
23. M.B. Shiflett and H.C. Foley: *Science*, 1999, vol. 285, pp. 1902–05.