

In summary, the scheme outlined in Fig. 1 is considered to be convenient for classifying polymorphic phase transitions in ceramics, inasmuch as it depends largely on experimental observations, i.e. the presence or absence of a latent heat, whether removal of this heat controls the growth of the product phase, and the presence or absence of a shape change.

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Elastic Moduli of Boron-Doped Silicon Carbide

W. S. COBLENTZ

SILICON carbide is a candidate material for gas turbine applications because of its high-temperature properties. Prochazka's¹ discovery of the sinterability of SiC has increased the economics of fabrication. The present study of elastic properties was undertaken as part of a materials development and characterization program for sintered SiC.

Elastic moduli data for SiC have been reported in the literature^{2–10}; however, Shaffer and Jun⁶ point out that much of these data are suspect because of the lack of sample characterization. The presence of lower-modulus phases reduces the observed elastic moduli of SiC. Calculated porosities are also in error if the theoretical density of SiC is used to obtain the porosity of material which is not single-phase. The effect of free Si is particularly noticeable in the high-temperature elastic moduli where it is responsible for the large decrease observed^{7,10} at $\approx 1350^\circ\text{C}$. The decrease in strength may be associated with a decrease in Young's modulus, since strength is a function of modulus.¹¹

Samples were prepared by 3 methods: (1) hot-pressed, (2) cold-pressed and sintered, and (3) injection molded with a wax vehicle, dewaxed, and sintered. Two lots of SiC powder were used; these powders contained 0.4% boron and 0.5% free carbon as sintering aids. The powders are characterized in Ref. 12. One percent of a binder (50% aluminum stearate and 50% oleic acid) was added as a pressing aid for the pressed samples.

Young's modulus was measured by determining the velocity of a longitudinal wave by the pulse-echo-overlap method.* Measurements to 1500°C were made using a 40-mil tungsten wave guide bonded into a small hole in the sample. The bonding agent used was made from $0.5\text{-}\mu\text{m}$ $\alpha\text{-Al}_2\text{O}_3$ powder and just enough $\text{Al}(\text{H}_2\text{PO}_4)_3$ solution to form a thick paste. Poisson's ratio was determined from the ratio of shear and longitudinal wave transit times in sintered blocks approximately 2 in. by 2 in. by 0.5 in. in the X, Y, and Z directions, respectively. Sample geometry allowed 3 independent pairs of measurements for each sample.

The experimental accuracy for the pulse-echo-overlap method was 0.5%. Accuracy for transit-time measurements was 0.05% for the Young's and shear moduli. Overall accuracy for both the pulse-echo-overlap technique and transit-time measurements is probably limited by sample uniformity. Spinner *et al.*¹³ have shown that the accuracy obtained for the elastic moduli of sintered materials decreases with porosity. Thus, for samples of polycrystalline ThO_2 , an accuracy of 1 to 4% was claimed, depending on porosity. The

Table I. Elastic Moduli Calculations

Method	Result for cubic SiC	Result for 6H polytype
Voigt	$E_v = 61.54 \times 10^6$ psi	$E_v = 66.25 \times 10^6$ psi
	$G_v = 26.414 \times 10^6$ psi	$G_v = 29.897 \times 10^6$ psi
	$V_v = 0.165$	$V_v = 0.108$
Reuss	$E_r = 54.861 \times 10^6$ psi	$E_r = 76.44 \times 10^6$ psi
	$G_r = 22.83 \times 10^6$ psi	$G_r = 31.76 \times 10^6$ psi
	$V_r = 0.201$	$V_r = 0.203$
Average	$\bar{E} = 58.20 \times 10^6$ psi	$\bar{E} = 71.346 \times 10^6$ psi
	$\bar{G} = 24.624 \times 10^6$ psi	$\bar{G} = 30.831 \times 10^6$ psi
	$\bar{V} = 0.1817$	$\bar{V} = 0.157$

measure of accuracy used was the agreement of Young's moduli calculated from flexural and longitudinal modes of vibration.

The data shown in Fig. 1 have been fit, by the least-squares approach, to exponential and quadratic equations:

$$E = 67.96 \times 10^6 e^{-3.21P} \text{ psi} \quad (1)$$

where $P = 1 - \rho/\rho_{th}$ and the standard deviation is 1.0×10^6 psi and

$$E = (69.79 - 294.32P + 1069.5P^2) \times 10^6 \text{ psi} \quad (2)$$

where the standard deviation is 1.3×10^6 psi. No difference could be found between Young's modulus for alpha and beta polycrystalline SiC, or between that of hot-pressed and sintered materials. Agreement with literature values is shown in Fig. 1.

The elastic moduli of fully dense polycrystalline SiC were calculated assuming random orientation (Table I). Single-crystal elastic constants calculated by Topolygo¹⁴ for cubic SiC were used because experimental values were not available. Single-crystal elastic constants measured by Arlt and Schodder¹⁵ were used for the calculations on the 6H polytype. Voigt and Reuss values assuming uniform local strain or stress, respectively, were calculated to give an upper and lower limit (equations for calculating polycrystalline elastic moduli can be found in Ref. 16). The calculated Young's modulus for theoretically dense cubic SiC is lower than that extrapolated from the present data; however, the calculated upper and lower

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The writer is with the Physical Chemistry Laboratory, The General Electric Company Research and Development Center, Schenectady, NY 12301.

*Measuring equipment from Panametrics, Waltham, MA.

¹ S. Prochazka, "Sintering of Dense Silicon Carbide," Rept. No. 74CRD067, General Electric Co., March 1974; to be published in *Proceedings of Ceramics for High Temperature Applications*, Hyannis, MA, November 1973.

² J. D. B. Veldkamp and W. F. Knippenberg, "Anomalous Young's Modulus of SiC at Elevated Temperatures," *J. Phys. D*, **7** [3] 407–11 (1974).

³ R. W. Bartlett, "Elastic Modulus of β -Silicon Carbide Whiskers," *J. Am. Ceram. Soc.*, **51** [2] 114–15 (1968).

⁴ E. Schreiber and N. Soga, "Elastic Constants of Silicon Carbide," *ibid.*, **49** [6] 342–44 (1966).

⁵ R. D. Carnahan, "Elastic Properties of Silicon Carbide," *ibid.*, **51** [4] 223–24 (1968).

⁶ P. T. B. Shaffer and C. K. Jun, "Elastic Modulus of Dense Polycrystalline Silicon Carbide," *Mater. Res. Bull.*, **7** [1] 63–70 (1972).

⁷ J. B. Wachtman, Jr., and D. G. Lam, Jr., "Young's Modulus of Various Refractory Materials as a Function of Temperature," *J. Am. Ceram. Soc.*, **42** [5] 254–60 (1959).

⁸ P. Kennedy and J. V. Shennan, pp. 359–66 in *Silicon Carbide—1973*, Edited by R. C. Marshall, J. W. Faust, Jr., and C. E. Ryan. University of South Carolina Press, Columbia, SC, 1974.

⁹ C. H. McMurtry, M. R. Kasprzyk, and R. G. Naum, pp. 411–19 in Ref. 8.

¹⁰ G. Q. Weaver and B. A. Olson, pp. 367–74 in Ref. 8.

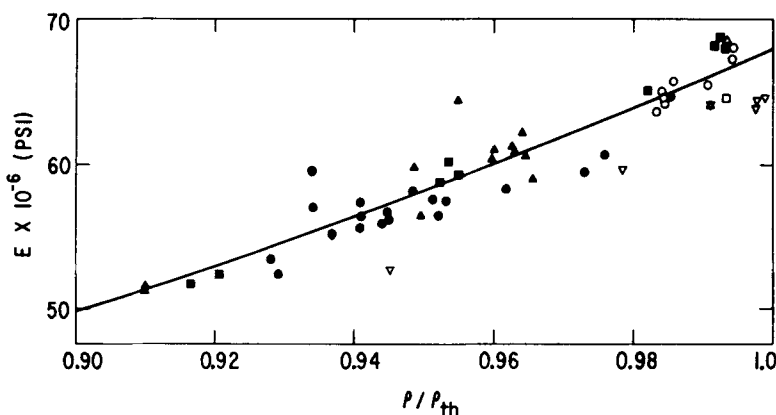
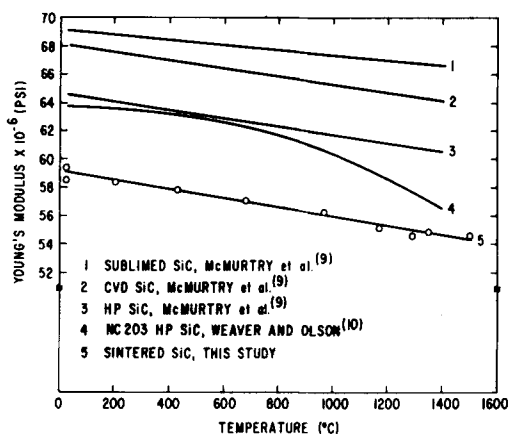


Fig. 1. Young's modulus of SiC at room temperature vs fraction of theoretical density; $\rho_{th} = 3.21 \text{ g/cm}^3$. Data from present study: (●) pressed and sintered, (▲) injection molded and sintered, (■) hot-pressed; (○) sublimed SiC (Ref. 6); (▽) HP-SiC (Ref. 5); (△) HP-SiC (Ref. 4); (◇) sublimed SiC (Ref. 9); (□) HP-SiC (Ref. 9); (○) CVD-SiC (Ref. 9).

Table II. Poisson's Ratio of SiC Blocks

Sample No.	ρ/ρ_{th}	Direction	Young's modulus ($\times 10^{-6}$ psi)	Shear modulus ($\times 10^{-6}$ psi)	Poisson's ratio
1*	0.965	X	53.034	22.7086	0.1675
		Y	52.864	22.647	.167
		Z	50.870	21.837	.165
2†	0.909	X	47.070	20.158	0.1675
		Y	47.074	20.114	.170
		Z	45.242	19.406	.1656
3‡	0.967	X	59.693	25.660	0.163
		Y	62.914	27.035	.163
		Z	60.159	25.844	.164

*84% cubic by X-ray, coarse grained (typical microstructure of sintered SiC described in more detail in Ref. 1), α plates, die-pressed. †Same microstructure as sample 1. ‡93% cubic by X-ray, fine grained ($\approx 2 \mu\text{m}$), isostatically pressed and sintered.

**Fig. 2. Young's modulus vs temperature.**

bounds for the 6H polytype bracket the extrapolated value. Scatter in the data (Fig. 1) is probably caused by an inhomogeneous porosity distribution which may result from the fabrication procedure. Injection-molded samples may show flow lines and die-pressed samples may have density gradients caused by pressure gradients. It is also conceivable that a high shrinkage rate could cause density gradients if the heating rate is fast enough and the heat transfer slow enough that the surface of the sample begins to sinter before the center of the sample does.

Modulus measurements on sintered SiC blocks are summarized in Table II. As with the pulse-echo measurements, sample inhomogeneity is apparent when the Young's and shear moduli differ in X, Y, and Z directions. The values for Poisson's ratio, $\mu = 0.165$, are low, relative to other carbides. Literature values^{4-6,10,17} for the Poisson's ratio of SiC vary from 0.168 to 0.225, with the lower values generally reported for the single-phase hot-pressed material.

The Young's modulus was measured as a function of temperature up to 1500°C (Fig. 2) for a sample of 96% theoretical density. Results are comparable to those of McMurtry *et al.*⁹ for α -SiC. There is no indication of any anomalous behavior, as reported by Veldkamp and Knippenberg² for α -SiC whiskers.

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¹¹ R. W. Davidge and A. G. Evans, "Strength of Ceramics," *Mater. Sci. Eng.*, **6**[5] 281-98 (1970).

¹² S. Prochazka and P. C. Smith, "Investigation of Ceramics for High-Temperature Turbine Vanes"; Report No. SRD-74-040, General Electric Co.

¹³ S. Spinner, F. P. Knudsen, and L. Stone, "Elastic Constant-Porosity Relations for Polycrystalline Thoria," *J. Res. Nat. Bur. Stand., Sec. C*, **67**[1] 39-46 (1963).

¹⁴ K. B. Topleygo, "Optical, Elastic and Piezoelectric Properties of Ionic and Valence Crystals with the ZnS Type Lattice," *Sov. Phys.-Solid State*, **2**[10] 2367-76 (1961).

¹⁵ G. Arlt and G. R. Schodder, "Some Elastic Constants of Silicon Carbide," *J. Acoust. Soc. Am.*, **37**[2] 384-86 (1965).

¹⁶ H. B. Huntington, pp. 317-18 in *Solid State Physics*. Edited by Frederick Seitz and David Turnbull. Academic Press, New York, 1958.

¹⁷ H. E. Rosinger, I. G. Ritchie, and A. J. Shillinglaw, "A Systematic Study of the Room Temperature Elastic Moduli of Silicon Carbide," *Mater. Sci. Eng.*, **16**[1-2] 143-54 (1974).

Electron Microprobe Analysis of Na₂O-CaO-SiO₂ Glass

D. E. CLARK,* L. L. HENCH,* and W. A. ACREE

PROBLEMS in the electron microprobe analysis of alkali glasses have been recognized by previous investigators.¹⁻⁵ Generally, the X-ray intensity for the alkali species changes as a function of time when an electron beam remains stationary on a glass specimen. An accompanying change in the X-ray intensities of other atomic species in the glass is also observed.³⁻⁴ This variation in X-ray intensity suggests a compositional change in the sample volume irradiated by the electron beam. Pantano *et al.*⁶ have reported similar changes in Na Auger electron intensities for alkali glasses subjected to a stationary beam. Plausible mechanisms associated with these local compositional changes are discussed by Lineweaver,¹ Borom and Hanneman,⁵ and Tanaka and Warrington.²

The surface condition of the glass specimen is also an important consideration in compositional analysis. Both abraded and corroded surfaces can cause considerable variation in X-ray intensities when the dimensions of the surface perturbations and the size of the electron beam are comparable. However, the capability for such analyses is important, especially in the container industry where glasses are subjected to corrosive environments.

The rate of alkali X-ray intensity change is proportional to the electron beam current, specimen temperature, and bulk composition of the glass under consideration. Small electron beam currents, low specimen temperatures, and the presence of Ca, Al, and Mg give correspondingly lower rates of alkali X-ray intensity change.⁷ Several methods for reducing the rate of change in alkali intensity are discussed in the literature.^{4,7-9} An electron raster technique has been used to stabilize the X-ray intensities of K₂O-SrO-SiO₂ glass long enough to obtain quantitative analysis.^{4,8} Moreover, it has been suggested that the change in X-ray intensities for alkali glass can be decreased by translating the specimen at a constant rate under a stationary beam.⁵ This note presents a method for obtaining reliable compositional analyses for a variety of Na₂O-CaO-SiO₂ glasses by utilizing electron beam enlargement and specimen translation. Because of its macroscopic nature, this technique is especially useful for analysis of abraded and corroded glasses.¹⁰

Several glasses were prepared by melting mixtures of reagent-grade NaCO₃, CaCO₃, and 0.5 μm SiO₂* at 1400°C for 24 h in a Pt crucible. The molten glass was pressed between graphite plates to a thickness of 3/8 in. and annealed at 450°C for 4 h. Specimens 3/4 in. square were polished to 600 grit with SiC paper for quantitative microprobe analysis. Polishing eliminates thin films and composition variations that may exist on the glass surfaces as a result of atmospheric corrosion. To evaluate the effect of surface roughness on X-ray intensity, similar samples were ground to 120, 240, 320, and 400 grit. The prepared samples were maintained in a desiccator until they were examined in the electron microprobe.[†]

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The writers are with the Ceramics Division, Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611.

*Member, the American Ceramic Society.

*Min-u-sil, Pennsylvania Glass Sand Corp., Pittsburgh, PA.

†Model Ms-64, Acton Laboratories, Inc., Acton, MA.

¹ J. L. Lineweaver, "Oxygen Outgassing Caused by Electron Bombardment of Glass," *J. Appl. Phys.*, **34**[6] 1786-91 (1963).

² S. Tanaka and D. H. Warrington, "Electron Microscope Observations of Thin Glass Foils," *Phys. Chem. Glasses*, **5**[3] 87-89 (1964).

³ R. V. Adams, H. Rawson, D. G. Fisher, and P. Worthington, "Use of Electron Probe X-Ray Microanalyser for Identification of Inhomogeneity in Glass," *Glass Technol.*, **7**[3] 98-105 (1966).

⁴ A. K. Varshneya, A. R. Cooper, and M. Cable, "Changes in Composition During Electron Microprobe Analysis of K₂O-SrO-SiO₂ Glass," *J. Appl. Phys.*, **37**[5] 2199 (1966).

⁵ M. P. Borom and R. E. Hanneman, "Local Compositional Changes in Alkali Silicate Glasses During Electron Microprobe Analysis," *ibid.*, **38**[5] 2406-2407 (1967).

⁶ C. G. Pantano, Jr., D. B. Dove, and G. Y. Onoda, Jr., "AES Analysis of Sodium in a Corroded Bioglass Using a Lower-Temperature Technique," *Appl. Phys. Lett.*, **26**[11] 601-602 (1975).

⁷ L. F. Vassamillet and V. F. Caldwell, "Electron-Probe Microanalysis of Alkali Metals in Glass," *J. Appl. Phys.*, **40**[4] 1637-43 (1969).

⁸ A. R. Cooper and A. K. Varshneya, "Diffusion in the System K₂O-SrO-SiO₂ I," *J. Am. Ceram. Soc.*, **51**[2] 103-106 (1968).

⁹ W. T. Kane, pp. 241-69 in *Microprobe Analysis*. Edited by C. A. Andersen. John Wiley & Sons, Inc., New York, 1973.

¹⁰ D. E. Clark, M. F. Dilmore, E. C. Ethridge, and L. L. Hench, "Aqueous Corrosion Behavior of Soda-Silica and Soda-Lime-Silica Glass," to be published in the *Journal of the American Ceramic Society*.