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The effect of small amounts of B and Sn on the sintering of silicon

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The sinterability of a Si powder, which undergoes limited densification at 1350° C, was remarkably influenced by small additions of B and/or Sn. Boron was shown to be a sintering aid and permitted the development of a fine-grain/fine-pore microstructure. Tin was shown to be sintering retardant and resulted in the formation of a highly-coarsened microstructure. The data presented supports the concept that B and Sn most likely affect the grain-boundary diffusion coefficient of Si.

1. Introduction

There is considerable technical and scientific interest in the sintering behaviour of fine Si powders. From a technical standpoint, dense polycrystalline Si may have a potential application as a support material for single-crystal Si wafers during high-temperature diffusion and oxidation processes. In addition, porous compacts of Si can be sintered to a desired final density before nitridation so that reaction-bonded Si_3N_4 may be formed with improved properties. Scientifically, Si has been identified as an excellent model material for studying the sintering of covalently-bonded solids [1] because much is known about the physical and chemical properties of both single-crystal [2, 3] and polycrystalline [4, 6] forms, including impurity diffusion data.

Recent papers [1, 7] on the sintering behaviour of "pure" Si revealed that submicron powders of specific surface area greater than $10\,m^2\,g^{-1}$ and at temperatures greater than 90% of the melting point, T_m, ($T_m \approx 1420°$ C) are required for powder compacts to undergo appreciable (> 5%) linear shrinkage on a macroscopic scale. Important conclusions deduced from these works have been that, in order to achieve high density during the sintering of Si, a high proportion of matter transport by volume and/or grain boundary diffusion (densifying mechanisms) must be maintained relative to proportion of matter transport through the vapour phase (non-densifying mechanism). If vapour transport dominates during sintering, the solid and pore phases coarsen dramatically via the disconnection of the solid phase at various points in the microstructure, leading to the development of a non-densifying microstructure. The pronounced dependence of densification on grain and pore growth during sintering has been theoretically developed [8].

The present paper investigates the effect of small additions of B and Sn on the sintering behaviour of a submicron Si powder having limited sinterability and on the corresponding development of microstructure. Boron and Sn were chosen as sintering additives for Si because thermodynamic, solubility and diffusion data for B and Sn available in the literature could be used to help understand some of the sintering results. Boron has a smaller atomic radius (0.88 Å) than that of Si (1.17 Å), a solubility limit of ≈ 0.46 wt % in Si at a temperature of 1350° C [10] and a diffusion coefficient [6] that is between 10 and 50 times greater in polycrystalline Si than in single-crystal Si. Tin, on the other hand, has a larger atomic radius (1.40 Å) [9] than Si, has a solubility limit of ≈ 0.43 wt % in Si at a temperature of 1350° C [10] and diffuses [11] into single-crystal Si at about the same rate as B, either alone, or simultaneously with B. It will be shown that a small amount of B acts as a densification aid but Sn, alone or in combination with B, drastically retards the sintering (densification) process.

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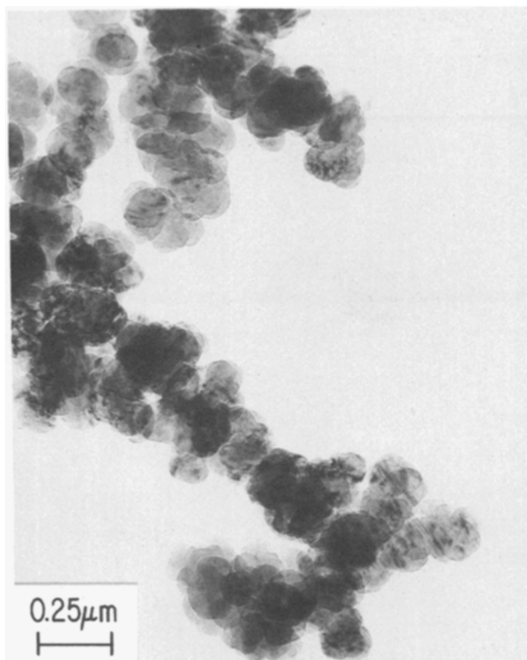
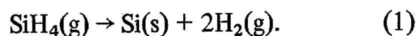


Figure 1 Typical TEM photomicrograph of particles of the starting SI powder.

2. Experimental procedure

Submicron Si powder of high purity was prepared by the thermal decomposition of silane, SiH_4, by the reaction



$$SiH_4(g) \rightarrow Si(s) + 2H_2(g). \quad (1)$$

The source of SiH_4 was a "calibration mixture" of 4 vol% SiH_4 and 96 vol% He*. A gas flow rate of $16 \text{ cm}^3 \text{ sec}^{-1}$ was used in a temperature gradient furnace at a maximum temperature of 650° C, after thoroughly purging the volume of the reaction chamber with Ar gas. The resulting Si powder (or smoke) was deposited on the inner wall of a fused silica tube placed in the furnace and exhibited a yellowish/dark-brown colour. The collected powder appeared to be inhomogeneous and, consequently, was annealed isothermally at 700° C in flowing Ar gas.

Characterization of the annealed Si powder showed that it was composed primarily of crystalline particles having a specific surface area of $14.6 \text{ m}^2 \text{ g}^{-1}$, corresponding to an average equivalent particle size of ~ 0.18 μm, and having an oxygen content ~ 0.4 wt %, which is assumed to be in the form of a thin SiO_2 layer on the particle surfaces. The size, shape and structure of the Si particles and agglomerates are illustrated in the TEM photomicrograph shown in Fig. 1. The dark streaks present in most of the Si particles suggest that these particles are crystalline and contain stacking faults. The cluster of particles shown in the bottom-central portion of Fig. 1 contains no internal structure, suggesting that they are amorphous. This latter observation is consistent with previous results [1] on other amorphous Si powders prepared by thermal decomposition of SiH_4. The majority of the individual particles are well-rounded and fall within a size range of 0.05 to 0.3 μm.

The chemical additives of elemental B and Sn were introduced either separately or simultaneously into the Si powder by mixing in a plastic jar with acetone for 0.5 h on a mixer/mill.† Another source of Sn tried was SnO_2. Concentrations of ≈ 0.4 wt % B and ≈ 0.43 wt % Sn, both alone and in combination, were chosen because these amounts are near the solubility limits [10] of B and Sn in Si at the sintering temperature of 1350° C.

Powder compacts 1 cm in diameter and 1 cm thick were prepared without binders by isostatically pressing about 0.7 g of powder at a pressure of $2 \times 10^8 \text{ Nm}^{-2}$. Specimens were placed on Al_2O_3 boats and sintered for 1 h at 1350° C in flowing argon ($10 \text{ cm}^3 \text{ sec}^{-1}$) which had been passed through an "oxygen-gettering" furnace before entering the sintering furnace. The effective partial pressure of O_2 was estimated to be approximately 10^{-7} atm.

The fired specimens were characterized for weight loss, shrinkage, density, microstructure, lattice parameter and chemical analysis by standard techniques.

3. Results and discussion

3.1. General observations on sintered silicon

The sintering results, presented in Table I, show that compacts of "pure" Si densify to only ~ 60% of the theoretical density (2.33 g cm^{-3}) and have an average linear shrinkage of 7.5% and a high weight loss of 5%. The addition of 0.4 wt % B to the Si powder causes pronounced macroscopic

*Union Carbide Corp., New York, NY, USA.

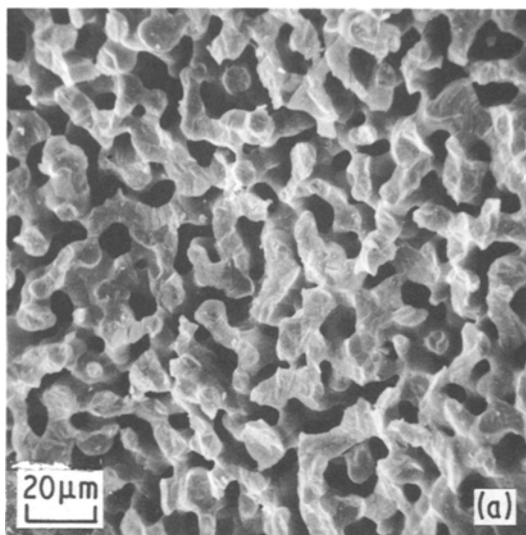
†Model 8000-11 manufactured by Spex Industries Inc., Scotch Plains, N.J., USA.

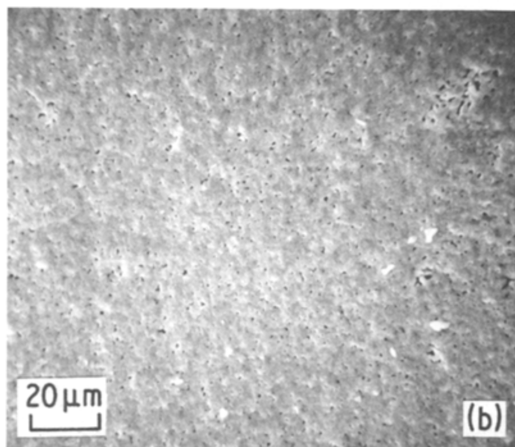
TABLE I Sintering results on Si compacts containing B and/or Sn additive and sintered at 1350° C for 1 h in argon. Relative green densities are approximately 40%.

Additive	Weight loss (%)	Relative density (%)	Linear shrinkage (%)
–	5.0	60	7.5
0.4 wt % B	2.3	86	17.3
0.4 wt % B + 0.55 wt % SnO_2	5.6	55	3.6
0.4 wt % B + 0.43 wt % Sn	5.0	58	5.5
0.43 wt % Sn	5.9	53	3.2
0.55 wt % SnO_2	6.3	56	4.4

densification to 86% and a much lower weight loss of 2.3%. Since the sintering temperature of 1350° C is below the Si–B eutectic temperature of 1392° C [12], sintering proceeds in the solid state. When 0.43 wt % Sin, either in the form of Sn or SnO_2, is added on its own or in combination with 0.4 wt % B, the sintering process (macroscopic shrinkage) is largely prevented or "poisoned" but high weight losses of 5 to 6% still occur. The addition of 0.43 wt % Sn to Si causes the appearance of a eutectic liquid at a temperature of 232° C [13] but at a high temperature of about ~ 1350° C a solid solution is expected to form [10]. These sintering results show clearly that a small amount of B acts as a sintering aid for Si whereas a small amount of Sn is a sintering retardant for Si.

A considerable amount of information about the sintering process can be obtained from observations on microstructure development in the sintered compacts of "pure" and doped Si. In Fig. 2a, the microstructure of poorly-sintered Si shows that the solid and pore phases are highly interconnected and have undergone extensive coarsening in comparison to the ultrafine microstructure (not shown) of the green compact. The average size of the solid and porous regions in sintered Si is about 8 μm, a value not much different from the 8.5 μm calculated for the equiv-





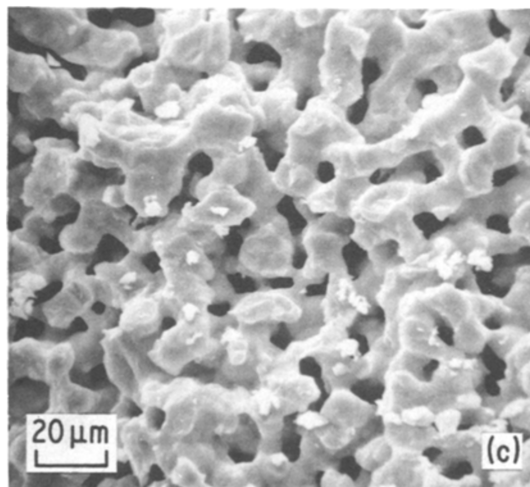


Figure 2 Typical microstructures revealed by SEM of fractured surfaces of compacts of (a) Si, (b) Si + 0.4 wt % B and (c) Si + 0.4 wt % B + 0.55 wt % SnO_2, sintered at 1350° C for 1 h in argon. White spots on fracture surfaces are contamination.

alent average diameter of the solid phase based on a specific surface area measurement of $0.3\,m^2\,g^{-1}$. Under the same experimental conditions, sintered Si containing 0.4 wt% B has a characteristically-different microstructure composed of ultrafine (~ 0.5 μm) grains and pores shown in Fig. 2b. This microstructure-type is typical of material which undergoes extensive macroscopic shrinkage (densification) during sintering. The simultaneous addition of 0.43 wt% Sn and 0.4 wt% B to the same Si powder results in the development of an "unsinterable" microstructure, shown in Fig. 2c, similar to that found for sintered, undoped Si.

3.2. The role of boron as a sintering aid

The sintering behaviour and microstructure development found for powder compacts of pure Si and of Si containing B and/or Sn additives can be interpreted in terms of the available information concerning the sintering of covalent solids [1, 7]. An important conclusion deduced in that previous work was that the development of "unsinterable" microstructures in pure Si, i.e. those microstructures which undergo extensive coarsening of the solid and pore phases, is a consequence of a high relative proportion of matter transport via vapour phase compared with the relative proportions transported by volume and/or grain boundary diffusion. The large weight loss of 5% observed in the present study for "unsinterable" compacts of Si and the known Si vapour pressure [14] of $\approx 4 \times 10^{-5}$ atm over Si at 1350° C both imply that considerable vapour transport of Si occurs during sintering. Addition of 0.4 wt% B to the same Si powder causes considerable densification to occur and results in the sintered material having a fine grain-fine pore microstructure. The vapour pressure of Si over solid Si containing 0.4 wt% B in solid solution is probably not much different than that for "pure" Si at 1350° C and, consequently, it cannot be argued that the observed increase in densification rate is due to decreased vapour transport.

The role of B in densification enhancement is probably related to an increase in the relative contribution to Si redistribution by grain boundary diffusion (rather than by volume diffusion) compared to redistribution by vapour transport. The reasoning behind this hypothesis is based on the following diffusion data for Si. The self diffusion coefficient of Si in single crystal Si containing ~ 0.2 wt% B in solid solution is about 2 times higher than the self diffusion coefficient of Si in pure Si at 1100° C [15]. This comparative result should not be markedly different for higher B concentrations at 1350° C and is too small to justify acceptance of the volume diffusion mechanism to explain the sintering enhancement observed. On the other hand, the diffusion coefficient of B in polycrystalline Si is 10 to 50 times larger than that in single-crystal Si [6]. This information, and the fact that the activation energy is lower for B diffusion in polycrystalline Si than in single crystal Si (2.51 and 3.42 eV, respectively) [6], suggest that grain boundaries play an important role in the diffusion process. It is known that B diffuses approximately 10 times faster than Si in single crystal Si [3], and B has been experimentally shown [15] and theoretically predicted [15, 16] to enhance the motion of Si atoms in its neighbourhood. It is therefore reasonable to expect that, during sintering, the diffusion coefficient of Si, the rate limiting species, is greatly enhanced along grain boundaries by the very mobile B atoms. Because of the ultrafine grain size of about 0.5 μm observed in sintered compacts of Si containing 0.4 wt% B, a large amount of grain boundary area per unit volume is available for this diffusion and lends further credence to the concept of accelerated diffusion of Si along grain boundaries.

3.3. The possible role of tin

This investigation has shown that the addition of 0.43 wt% Sn to a Si powder or to a powder mixture of Si containing 0.4 wt% B causes major inhibition of densification during sintering of powder compacts. A better understanding of the role of Sn can be obtained from data on lattice parameters and linewidths, obtained from X-ray studies, for sintered samples and from diffusion data for Sn in Si. In Table II the lattice parameter for the cubic, diamond structure of Si is 5.4304 Å for "pure", sintered Si and is virtually identical to that measured for a National Bureau of Standards Si standard. Sintered material containing 0.4 wt% B has a smaller lattice parameter of 5.4250 Å because the smaller B atoms (0.88 Å) enter into substitutional solid solution with the larger (1.17 Å) Si atoms. The X-ray line broadening of the (4 4 4) reflection of the B-doped Si sample was about 75% larger than that of "pure" sintered

TABLE II Results from X-ray diffraction studies of samples containing Si and various additions sintered at 1350° C for 1 h in argon.

Composition	Lattice parameter*, a_0 (Å)	Linewidth†, $\Delta\theta$
Si (NBS Standard)	5.4304 ± 0.0003	–
Si	5.4304 ± 0.0002	1
Si + 0.4 wt % B	5.4259 ± 0.0006	1.75
Si + 0.4 wt % B	5.4260 ± 0.0008	1.75
Si + 0.4 wt % B + 0.55 wt % SnO_2	5.4239 ± 0.0002	1.50
Si + 0.4 wt % B + 0.43 wt % Sn	5.4236 ± 0.0002	1.50
Si + 0.43 wt % Sn	5.4305 ± 0.0002	1.20

*Determined by the Debye–Scherrer method.
†Determined from a microdensitometer profile of the (4 4 4) reflection.

Si and is probably associated with uniform lattice strain related to the difference in the size of the B and Si atoms in solid solution and/or related to compositional variations within the single-phase solid solution because of poor initial mixing and, subsequently, incomplete interdiffusion of the B and Si atoms. The addition of 0.43 wt % Sn, in the form of either Sn or SnO_2, to B-doped Si results in sintered material having nearly the same lattice parameters, but these are significantly lower than those of Si samples containing 0.4 wt % B only. Furthermore, the linewidth of the (4 4 4) reflection for sintered samples containing both B and Sn was approximately 50% larger than that for pure, sintered Si but noticeably smaller than that for sintered Si containing B only. These results suggest that large (1.40 Å) Sn atoms dissolve at least partly along with the small B atoms into the Si lattice. To account for the smaller lattice parameter of Si containing B and Sn compared with that of Si with B only, apparently Sn either enhances the solubility of B in Si or prevents B from precipitating out of solid solution in the form of B_4Si during cooling from the sintering temperature. Qualitative chemical analysis of sintered Si containing 0.43 wt % Sn and 0.4 wt % B, using a SEM equipped with a solid state X-ray detector, confirmed the presence of residual Sn in the sample. The lattice parameter of 5.4305 Å found for sintered Si containing 0.43 wt % Sn was unexpectedly similar to that of pure, sintered Si considering the solubility [10] of Sn in Si at 1350° C. This X-ray result indicates that a substantial portion of the Sn solute may have precipitated from a supersaturated solid solution during cooling from the sintering temperature.

The drastic reduction in sinterability (densification) of compacts of B-doped Si powder caused by the presence of a small amount of Sn is probably related to an "association effect" of the B and Sn atoms which results in decreased diffusivity of Si along the grain boundaries. That is, it is postulated that the larger Sn atoms and the smaller B atoms segregate at the Si grain boundaries in order to minimize lattice strain effects. Localized coupling of the B and Sn atoms would reduce the effective mobility of the former and thereby also decrease the ability of B to increase Si self-diffusion in grain boundaries. This postulate is supported by diffusion data for Sn into Si. The diffusion of Sn in nearly-intrinsic single-crystal Si at temperatures between 1050 and 1200° C results in substantial lattice strain and Sn surface pile-up [11]. The extrapolated diffusion coefficient of Sn in Si at 1350° C is approximately 2×10^{-12} cm^2 sec^{-1} and is nearly equal to that for self-diffusion of Si in Si [11]. Furthermore, in the simultaneous diffusion of Sn and B into single-crystal Si, the diffusion coefficient of Sn is found to be nearly the same as that without B [11]. Unfortunately, data on B diffusion in the presence of Sn in Si is unavailable. If it transpires that the diffusion coefficient of B is reduced by the presence of Sn impurity in Si, then this would lead to a decrease in the diffusivity of Si according to arguments put forward in [16], and lend further support to the postulate made above.

The above discussion has centred on the possible reasons why Sn affects and reduces Si diffusion rather than increases the rate of vapour transport of Si. It must be pointed out that vapour transport does occur at 1350° C, as indicated by the high weight losses shown in Table I. However, even if the Si vapour pressure increases locally at the interparticle (intergrain) contact points by as much

as a factor of 2 or 3 because of a small amount (< 1 wt%) of eutectic liquid possible for the present composition, this would probably not account for the very large changes observed in the sintering rate and microstructural transformation.

4. General comments

The preparation of covalent substances such as Si, SiC, Si_3N_4 and AlN having high density and fine-grain size usually requires the use of sintering aid(s) and high temperature to speed-up the sintering kinetics. One type of sintering aid causes liquid formation, and examples are the addition of 1 to 5 wt% of MgO [17] or 10 to 25 wt% of Al_2O_3 + AlN [18] to Si_3N_4. Another type of sintering aid(s) appears to operate via solid-state diffusional processes. One example of the latter kind of aid is the addition of a small amount (< 1 wt%) of B + C to SiC [19]. A recent sintering study [20] of β-SiC showed evidence for the existence of a grain boundary phase, rich in B and C, through which rapid diffusion of Si and C could occur during densification. The present investigation on the sintering of B-doped Si compacts also revealed strong, indirect evidence supporting the suggestion of grain-boundary diffusion as the dominant mechanism operating during sintering. These sintering studies on covalently-bonded solids tend to suggest that effective sintering additives are those additives that change grain boundary chemistry either by forming reactive liquid phases or by producing solute segregation effects. Therefore, understanding grain boundary chemistry (reactions, composition, structure) is essential to the understanding of the sintering behaviour of covalent solids.

Finally, it should be noted that the role of the oxygen impurity of 0.4 wt% found in the starting Si powder on the subsequent sintering of powder compacts with and without the B and Sn additives is not known. Typically, the oxygen is present in the form of an amorphous SiO_2 film on the surfaces of the Si particles. Chemical reaction(s) between the surface SiO_2 and the sintering additive(s) during the densification process may occur and affect the sintering rate. Nevertheless, a significant amount of oxygen loss is expected to occur during sintering via SiO formation and evolution because of the expected self reduction of SiO_2 by Si [21] and the low partial pressure of oxygen (~ 10^{-7} atm) prevailing in the sintering atmosphere at 1350° C. Although the maximum solubility of oxygen in Si is about 20 ppm at the melting point [2], the effect of higher concentrations of oxygen on the sintering rate and solubility in polycrystalline Si is so far unknown and represents an area for further research.

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References

1. C. GRESKOVICH and J. H. ROSOLOWSKI, *J. Amer. Ceram. Soc.* 59 (1976) 336.
2. A. J. R. DeKOCK, Philips Research Report Supplement No. 1, 1973, pp. 1–105.
3. D. L. KENDALL and D. B. DeVRIES, in "Semiconductor Silicon" edited by R. R. Haberecht and E. L. Kern (The Electrochemical Society Inc., New York, 1969) pp. 358–403.
4. C. C. MAI, T. S. WHITEHOUSE, R. C. THOMAS and D. R. GOLDSTEIN, *J. Electrochem. Soc.* 118 (1971) 331.
5. T. I. KAMINS, J. MANOLIU and R. N. TUCKER, *J. Appl. Phys.* 43 (1972) 83.
6. S. HORIUCHI and R. BLANCHARD, *Solid-State Electron.* 18 (1975) 529.
7. C. GRESKOVICH, S. PROCHAZKA and J. H. ROSOLOWSKI, in "Nitrogen Ceramics" edited by F. L. Riley (Noordhoff Publishing, Alphen aan den Rijn, The Netherlands, 1977) p. 351.
8. J. H. ROSOLOWSKI and C. GRESKOVICH, *J. Amer. Ceram. Soc.* 58 (1975) 177.
9. L. PAULING, "The Nature of the Chemical Bond" 3rd ed. (Cornell University Press, New York, 1960) p. 256.
10. F. A. TRUMBORE, *Bell System Tech. J.* 39 (1960) 205.
11. T. H. YEH, S. M. HU and R. H. KASTL, *J. Appl. Phys.* 39 (1968) 4266.
12. C. GRESKOVICH, unpublished work (1976).
13. M. HANSEN, "Constitution of Binary Alloys" 2nd edn. (McGraw-Hill Book Co. Inc., New York, 1958) p. 1194.
14. Y. M. SHASHKOV, "Metallurgy of Semiconductors" (Consultants Bureau, New York, 1961) p. 3.
15. J. M. FAIRFIELD and B. J. MASTERS, *J. Appl. Phys.* 38 (1967) 3148.
16. R. E. HOFFMAN, D. TURNBULL and E. W. HART, *Acta Met.* 3 (1955) 417.
17. G. R. TERWILLIGER and F. F. LANGE, *J. Mater. Sci.* 10 (1975) 1169.
18. M. MITOMO, N. KURAMOTO and Y. INOMATA, *ibid.* 14 (1979) 2309.

19. S. PROCHAZKA, in "Special Ceramics 6" edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1975) p. 171.
20. H. SUZUKI and T. HASE, in Proceedings of the International Symposium on Factors in Densification and Sintering of Oxide and Non-Oxide Ceramics, edited by S. Sōmiga and S. Saito, (Gakujutsu Bunken Fukyu-Kai, Tokyo, 1979) p. 345.
21. D. R. STULL and H. PROPHET, JANAF Thermochemical Tables, 2nd edn., National Bureau of Standards Publication Number NSRDS-NBS 37, June, 1971.

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