# Effect of Crystallization of the Grain-Boundary Phase on the Thermal Diffusivity of a Sialon Ceramic

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*Crystallization of the glassy grain-boundary phase in a series of sialon ceramics fabricated using a range of hot-pressing schedules increased the thermal diffusivity at room temperature by an average of $\approx 10\%$. For samples made by a given hot-pressing schedule, the relative difference in thermal diffusivity between composites containing a glassy grain-boundary phase and those in which this phase had crystallized decreased with increasing temperature. This behavior is attributed to enhanced phonon scattering in the crystalline grain-boundary phase.*

THE DENSIFICATION during sintering of polycrystalline ceramics for high-performance applications can be enhanced significantly by the addition of a sintering aid. This is particularly so for $Si_3N_4$-based ceramics, which do not densify readily without the assistance of additives. For $Si_3N_4$, additives commonly consist of the oxides of magnesium, yttrium, or aluminum. At the fabrication temperatures, the presence of these additives results in the formation of a liquid phase at the grain boundaries. This liquid phase can act either as a lubricant to promote particle transport or as a medium for material transport by solution and reprecipitation of the matrix phase. On cooling, the liquid at the grain boundaries and triple points becomes a glass.

The presence of this grain-boundary

phase, which can vary from just a few percent to over 10%, is expected to have an effect on the continuum properties of the final densified product. This effect is well known for mechanical behavior, especially at temperatures sufficiently high that the grain-boundary phase can undergo significant viscous deformation.

The effect of the grain-boundary phase on the continuum properties of polycrystalline aggregates also is expected to be a function of the degree of crystallinity. In terms of the objectives of this study, note that glassy (amorphous) materials generally exhibit a much lower thermal conductivity and diffusivity than their crystalline counterparts of identical composition[1,2] because of enhanced phonon scattering. A polycrystalline ceramic with a grain-boundary phase can be considered to be a composite. Cheng and Vachon[3] reported that the thermal conductivity of composites is a function of the thermal conductivity, volume fraction, and distribution of each component. Continuous phases are particularly effective in affecting the thermal conductivity of composites. For this reason, the presence of a grain-boundary phase and the degree of its crystallinity are expected to have a significant effect on the thermal transport properties of polycrystalline aggregates.

Experimental data are presented in support of this hypothesis.

## EXPERIMENTAL PROCEDURE

The materials for this study consisted of a $\beta$-sialon ($\beta$-$Si_3N_4$ solid solution containing 5 eq% Al, i.e. $\beta$-$Si_{6-x}Al_xO_xN_{8-x}$ where $x = 0.4$) with $\approx 10$ wt% grain-boundary phase corresponding to the composition of the mineral garnet, i.e. $Y_3Al_5O_{12}$ (Ref. 4). The samples were prepared by hot-pressing appropriate mixtures of powders of $Si_3N_4$,* $AlN$,[†] $Al_2O_3$,[‡] and $Y_2O_3$[§] in BN-coated graphite dies at a pressure of $\approx 20$ MPa in nitrogen from 1550° to 1690°C for periods from 15 to 120 min. The densities achieved were at least 99.5% of theoretical. After the samples were hot-pressed, they were annealed at 1350°C for 20 h, which resulted in nearly complete crystallization of the garnet grain-boundary phase. Details of the X-ray and transmission electron microscopy studies of the crystallization process are presented in Ref. 4. In the "as-hot-pressed" samples, $\beta$-sialon was the only crystalline phase, whereas garnet was the only second crystalline phase in the annealed specimens.

The effect of the crystallization of the grain-boundary phase on thermal transport behavior was determined by measuring thermal diffusivity by the flash method[5] using a glass-Nd laser as the source. The specimens for these measurements consisted of plates $\approx 6$ mm square and $\approx 1.5$ mm thick. Room-temperature measurement of thermal diffusivity was conducted in air; at high temperatures, specimens were contained in a carbon fur-

Fig. 2. Temperature dependence of thermal diffusivity of $\beta$-sialon/garnet hot-pressed at 1690°C for 30 min compared to that of $\beta$-sialon/garnet hot-pressed under same conditions and then annealed at 1350°C for 20 h. Curves represent linear least-squares fits of measured thermal diffusivity to reciprocal absolute temperature.
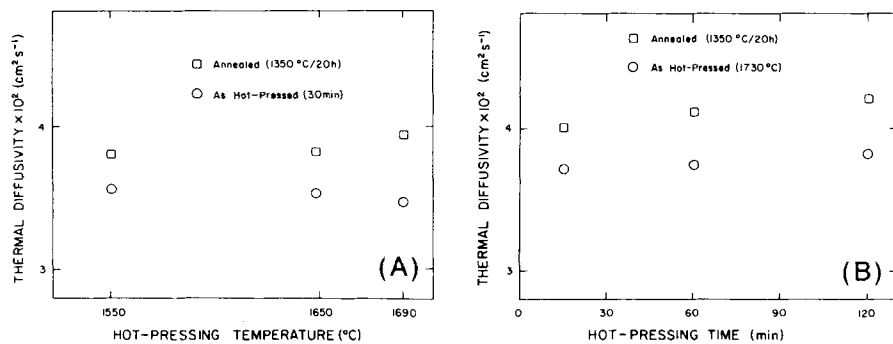


Fig. 1. Effect of annealing at 1350°C for 20 h on room-temperature thermal diffusivity of $\beta$-sialon/garnet (A) hot-pressed at varied temperatures for 30 min and (B) hot-pressed at 1730°C for varied times.
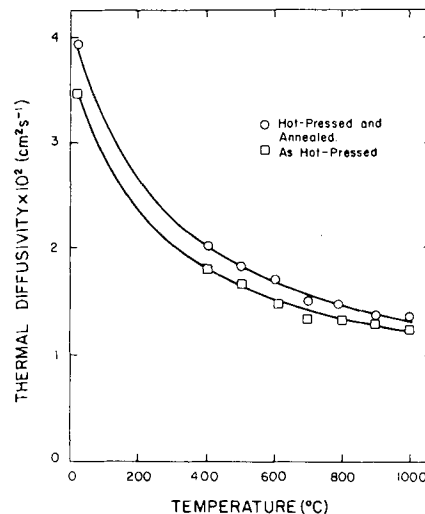
nace with a protective nitrogen atmosphere. The direction of heat flow in the specimens was parallel to the hot-pressing direction.

## RESULTS AND DISCUSSION

Figure 1(A) compares the data for the thermal diffusivity at room temperature before and after the annealing of samples hot-pressed for 30 min at varied temperatures. Similarly, Fig. 1(B) compares the corresponding data for specimens hot-pressed at 1730°C for varied time periods. Both sets of data show an ≈10% increase in the thermal diffusivity after annealing, regardless of the hot-pressing conditions.

Figure 2 compares the temperature dependence of the thermal diffusivity for sialon samples with a glassy and a crystalline grain-boundary phase. Both samples were hot-pressed for 30 min at 1690°C. The relative difference in the thermal diffusivity decreases with increasing temperature. This decrease is ex_ ' since enhanced phonon scattering generally produces a greater relative decrease in the thermal conductivity and diffusivity of crystalline materials than for glassy materials. The data in Fig. 2 were obtained up to 1000°C to avoid crystallization of the grain-boundary phase at higher temperatures. Such crystallization would lead to a permanent increase in the thermal diffusivity of the "as-hot-pressed" sample if measurements had been conducted to temperatures as high as 1200° or 1300°C. Although the temperature dependence of the thermal diffusivity was measured for only one hot-pressing condition, it is anticipated that the samples for the other hot-pressing conditions would exhibit a behavior similar to that shown in Fig. 2.

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# Cation Valence in VOx

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By comparing the position of the K absorption edge of VOx to that of V metal, $V_2O_4$, and $V_2O_5$, it is concluded that the cation in VOx has the classical valence of 2 + only for oxygen-rich compositions.

THE CONCEPT of classical valence plays a key role in the defect chemistry of non-stoichiometric oxides. Yet many of these materials are semiconductors or metallic in their behavior.

The oxide VOx ($0.75 < x < 1.3$) is one such example; it is metallic for vanadium-rich compositions and a semiconductor for oxygen-rich material.[1] Theoretical calculations[2-4] and experiments involving combined X-ray diffraction and high-voltage electron microscopy (critical voltage and disappearing Kikuchi lines[5,6]) suggest that the valence is less than the classical value of 2+. Furthermore, although it is assumed generally that vacant cations produce a higher valence on some of the remaining cations, in at least one carbide, charge compensation appears to occur by a decrease in the anion valence.[7] The purpose of this communication is to probe the cation valence in VOx (at three compositions) by examining the chemical shift of the K absorption edge of vanadium.

## EXPERIMENTAL PROCEDURE

A description of the preparation of the VOx samples is given in Ref. 6. Crystals were ground to a powder and coated on adhesive tape. Three such tapes were superimposed to obtain suitable X-ray absorption and mounted on a cardboard frame. Similar samples were prepared from high-purity $V_2O_4$, $V_2O_5$, and annealed filings of vanadium metal.

Near-edge spectra, shown in Fig. 1, were obtained using a 12-kW rotating anode generator† with Mo target operating at 30 kV, 160 mA. The energy of the radiation was selected by the 220 reflection from a thin Si slice bent elastically to focus the radiation at a slit used to improve the energy resolution. The bending jig was mounted on a diffractometer‡ in a helium atmosphere. A sample was placed downstream from the slit, and the beam intensity was measured (simultaneously) before and after it entered the sample with gas-flow detectors. The incident-beam detector was smaller than that for the transmitted beam, and the gas pressure was adjusted to absorb only 10% of the beam. The output of this detector was used in a feedback circuit to maintain a constant intensity incident on the sample for all energies. (A more complete description of the apparatus is given in Ref. 8.) A 100-eV range around the vanadium metal absorption edge was sampled for 30 s at 0.5-eV intervals. The range from 5430 to 5730 eV was recorded at 5-eV steps, each for 10 s. The absorption-edge jump height was obtained by curve-fitting the pre- and post-edge portions of the extended spectra, and the detailed spectra for all samples were normalized such that the absorption jump equals unity. The position of the edge was found from the derivative of the (normalized) data, ignoring any pre-edge peaks. Data acquisition and processing were controlled by a microcomputer system.§

## RESULTS AND DISCUSSION

In Fig. 2, the normalized absorption coefficient and its derivative are shown for V metal. The edge is at 2.72 eV from (the arbitrary) zero; the first maximum in the derivative is a pre-edge peak. The shifts were correlated with the coordination charge ($CC$) because previous work[9-11] has indicated a linear relation. Coordination charge is defined as:

$$CC = ml \qquad (1)$$

where $m$ is the valence and $I$ the ionicity calculated from the Pauling formula[12]:

$$I = 1 - \exp\left[-(1/4)(X_V - X_O)^2\right] \qquad (2)$$

where $X_V$ and $X_O$ are V and O electronegativities (having values of 1.63 and 3.44, respectively[13]). The results are shown in Fig. 3 in which the straight line is drawn through the points for V, $V_2O_4$, and $V_2O_5$. The coordination charges were obtained from the measured edge shifts for $VO_{0.80}$, $VO_{1.02}$, and $VO_{1.25}$ in Fig. 3, and valence results (Table I) were determined using Eqs. (1) and (2). The quoted errors arise from the uncertainty in the straight line fit in Fig. 3 and from uncertainties in locating the peaks in the derivative spectra.

It is clear that in VOx, the valence only approaches the classical value of 2+ in the most oxygen-rich compositions, in agree-