Synthesis of Lithium Ion Conductor, γ_s-$Li_{3.4}Si_{0.4}V_{0.6}O_4$, by the Alkoxide Method

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This paper describes a new preparation process of highly densified bodies of a γ_s-$Li_{3.4}Si_{0.4}V_{0.6}O_4$ solid solution, which is the best lithium ion conductor among those containing silicates, via sintering a xerogel powder derived from alkoxides. The xerogel powder consisting of spherical, amorphous aggregates was prepared by hydrolysis of alcoholic solutions of $Si(OC_2H_5)_4$, $VO(OC_2H_5)_3$ and $LiOC_2H_5$ at 70°C, followed by drying. The diameter was smaller than 0.1 μm. The powder crystallized gradually into the β_s-solid solution with poor crystallinity above 500°C, and a γ_s-solid solution appeared above 650°C. The highly densified bodies of the γ_s-solid solutions were obtained by sintering the compact of the xerogel powder at a relatively low temperature, 900°C. The sintered bodies consisted of only the γ_s phase and contained no other phases such as Li_4SiO_4 which forms as a result of Li_2O evaporation during sintering. This method lowered the sintering temperature by 150°C compared with that for the conventional method. The ionic conductivities of the sintered bodies were determined by analysing their complex impedance diagrams in the frequency range of 5 Hz-13 MHz. The sintered bodies prepared by the conventional method were characterized by the presence of two distinct semicircles in the complex impedance diagram; one corresponds to AC response of the grain (bulk) and the other to that of the grain boundaries. However, the sintered bodies prepared by this method indicated only a single semicircle due to AC response of the grain. The total ionic conductivity of the sintered bodies, 3.4×10^{-5} Scm^{-1} at 25°C rising to 4.7×10^{-3} Scm^{-1} at 150°C, was about three times higher than that of the those prepared by the conventional method due to negligible grain boundary resistance. [*Received July 15, 1986*]

Crystallization of Mullite-Zirconia Amorphous Materials Prepared by Rapid-Quenching

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Amorphous materials have been prepared by rapid quenching, ~10^5°C/s, of the melt of the mixed oxides, 20wt% ZrO_2-80wt% (3.4 Al_2O_3·2 SiO_2) using an arc-imaging furnace and a twin-roller. This paper deals with the crystallization and the products of these amorphous materials obtained by reheating under various conditions. The crystallization of this amorphous material took place at ~990°C precipitating t-ZrO_2 and mullite phases after showing glass-transition temperature at 919°C on heating by 10°C/min. The mullite had markedly larger lattice parameters than that of stoichiometric mullite (3 Al_2O_3·2 SiO_2) indicating higher (>83wt%) Al_2O_3 contents in the early stage of crystallization, then showed smaller lattice parameters on prolonged reheating. The TEM observation of the sample re-heated at 1200°C for 12 h revealed that the product consists of mullite grains of 2-5 μm in which fine (10-20 nm) t-ZrO_2 crystals are contained. The characteristic arrangements of the fine ZrO_2 crystals in the mullite grains suggest that these t-ZrO_2 crystals are precipitated by exsolution on the crystallization of the mullite from the amorphous matrix. Reheating of the amorphous materials at 880°C reduced the glass-transition and crystallization temperatures and increased the lattice parameters of mullite. This suggests that the heat treatment at 880°C caused a phase separation in amorphous samples. The phase separation would yield the precipitation of Al_2O_3-rich mullite in the early stage of crystallization with the exsolution of t-ZrO_2 micro-crystals. [*Received July 14, 1986*]

HIP Sintering of Silicon Carbide without Additives

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Eight kinds of commercial SiC powders were cold pressed isostatically, encapsulated in a silica glass tube, and HIPed in 150 MPa-argon gas at 1900°-2000°C. The density, microstructure, hardness and K_{IC} were studied. The results are summarized as follows:

(1) The density of sintered specimens depends strongly on the mean particle size of starting powders and HIP temper-

ature. High density (>99.7% T.D.) was obtained by HIPing above 1950°C using powders with the mean particle size less than 0.6 μm. With 0.8 μm α-SiC powder, the sintered density was about 95% T.D. with slight dependence on the HIP temperature.

(2) The microstructure of highly dense sintered materials was uniform with fine grains, but that of 95% T.D. material was characterized by coarse grains and intra-granular isolated pores.

(3) α-SiC powder sinters better than β-SiC powder for the same mean particle size.

(4) Fine SiC powders gave high Vickers hardness and low K_{IC} value in comparison to coarse powders.

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HIP Sintering of Silicon Nitride without Additives

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Four kinds of Si_3N_4 starting powders with different amounts of impurities and various specific surface areas, were cold pressed isostatically, encapsulated in a Vycor glass tube, and HIPed in 150 MPa-argon gas at 1800°-2000°C. The density, flexural strength, hardness and microstructure were investigated. The results are summarized as follows:

(1) Sintered materials with more than 99% relative density were fabricated by HIPing above 1900°C.

(2) The sintered materials were composed of equiaxed β-Si_3N_4 grains. A small amount of an intergranular glassy phase was detected using high resolution TEM technique.

(3) The sintered materials prepared from high purity powders showed excellent mechanical properties at elevated temperature, i.e. the flexural strength at 1400°C and Vickers hardness at 1300°C were 750 MPa and 13.2 GPa, respectively.

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Very High Pressure Hot Pressing of Oxidized Silicon Nitride Powders without Additives

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Silicon nitride powders operated by oxidation in air at 1200°C for 70 to 210 min, in which the oxygen content was from 2.8 to 8.9 wt%, were sintered without additives under the pressure of 3.0 GPa. The influence of oxygen on the characteristics of the sintered bodies was studied. Various amounts of α phase remained in sintered bodies depending on the oxygen content in the operated powders. Vickers microhardness of the sintered body prepared from the powder containing 2.8 wt% oxygen was higher than that of the sintered body from the starting powder at elevated temperature up to 1300°C.

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Synthesis and Reaction Sintering of WB

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The conditions for preparing WB by solid state reaction between tungsten and amorphous boron powders were investigated. The effect of added titanium or zirconium on the sinterability of the synthesized WB powder was examined under high pressure and temperature conditions. WB was obtained as a single crystalline phase, when a mixed powder containing boron 10