Preparation of Tetragonal Zirconia Containing Glass-Ceramics and Its Mechanical Properties

Osamu SAKAMOTO and Masayuki YAMANE*

Research & Development Division, Asahi Glass Co., Ltd.
Hazawa-cho, Kanagawa-ku, Yokohama-shi 221
* Department of Inorganic Materials, Tokyo Institute of Technology

Glass-ceramics containing tetragonal ZrO_2 *(t-*ZrO_2*) have been prepared and their mechanical strength and fracture toughness were measured. Glasses containing up to 15 mol%* ZrO_2 *in the ternary system* SiO_2*-CaO-*ZrO_2 *changed to glass-ceramics containing CaO·*SiO_2*, 2 CaO·*ZrO_2*·4* SiO_2 *and a small amount of t-*ZrO_2 *by the heat-treatment at 900°-1200°C for 1-24 h. These glass-ceramics, however, had large cracks inside the bodies due to the growth of fibrous CaO·*SiO_2 *and 2 CaO·*ZrO_2*·4* SiO_2 *crystal from surface. On the other hand, addition of 5 mol%* P_2O_5 *to the 50* SiO_2*·38 CaO·12* ZrO_2 *composition led to bulk crystallization resulting in the formation of crack-free glass-ceramics. The crystallization mechanism was investigated by SEM, EPMA and X-ray diffraction. It was found that the glass containing 5 mol%* P_2O_5 *formed* SiO_2*-rich droplets 1-2 μm in diameter on cooling from melt. When the glass was heat treated above 860°C, 4 CaO·*P_2O_5 *crystal 50-100 nm in diameter precipitated first in the matrix of the phase separated glass, and then t-*ZrO_2 *crystal 30-35 nm precipitated around* SiO_2*-rich droplets as a major crystalline phase at a temperature above 900°C. This t-*ZrO_2 *did not transform to monoclinic* ZrO_2 *by heat-treatment at 910° and 1070°C for 48 h. Young's modulus, mechanical strength, fracture toughness and fracture energy of the glass and glass-ceramics were measured by sing-around method, three-point bending method, indentation method and work of fracture method, respectively. Although the increase of Young's modulus was very small, the strength, fracture toughness and fracture energy increased considerably by the precipitation of t-*ZrO_2*.*

[Received July 3, 1985]

Synthesis of Spherical Silica Particles and Their Thermal Behavior

Yasuo AZUMA, Yoshimi TAJIMA, Nobuo ŌSHIMA and Kensuke SUEHIRO

Department of Industrial Chemistry, Faculty of Engineering, Tokai University
Kitakaname, Hiratsuka-shi 259-12

Spherical silica particles were prepared by the hydrolysis of orthoethyl silicate in a alcoholic solution in the presence of ammonia catalysis. The thermal behaviors of the obtained spherical particles were examined by TEM, TG-DTA, IR and XRD. Results obtained were as follows.

(1) The hydrolysis product of orthoethyl silicate was homogeneous and truly spherical. Their diameters were changed by the mol ratio $H_2O/Si(OC_2H_5)_4$*,* $NH_3/Si(OC_2H_5)_4$ *of the solution and the reaction temperature.*

(2) By heat treatment, the combustion of organic matters in silica occurred at about 400°C, and the dehydration from silanol group at nearly 450°C. The autoclave treatment removed the organic matters from silica particles and decreased silanol group. The Si-O bond became strong.

(3) By heat treatment, the density approached to that of silica glass and the specific surface area decreased. But the autoclave treatment, its density and specific surface area remained unchangéd, but the autoclaved powder was highly dispersive in alcohol.

[Received May 29, 1985]

Thermal Shock Behavior of Y_2O_3-Partially Stabilized Zirconia

Masahiro ASHIZUKA, Yasuyuki KIMURA, Hideki FUJII, Kouichi ABE and Yoshitaka KUBOTA

Kyushu Institute of Technology
1-1, Sensui-cho, Tobata-ku, Kitakyushu-shi 804
* Toyo Soda Manufacturing Co., Ltd.

The thermal shock behavior of 3 mol % Y_2O_3*-partially stabilized zirconia with average grain size of 0.4 μm (Z3Y-I) and 1.0 μm (Z3Y-II) has been studied by the water quench method. Twenty three specimens of rectangular cross-section* *bar (3 by 3 by 45 mm) were quenched at 300°, 350° and 400°C temperature differentials (ΔT) and their retained strength (σ_f) were plotted using the Weibull distribution function and doubly exponential distribution function. The retained strength distribution at $\Delta T = 350°C$ are similar to the original strength distribution. On the other hand, the distribution at $\Delta T =$ 350° and 400°C showed a shoulder at $F = 0.458$ and 0.875, respectively. They are the initiation points of thermal shock damage. Assumming the surface heat transfer coefficient (h) of 0.19 and 0.4 cal/cm²·°C·s, calculated stress intensity factors K_I's for crack initiation by water quench were 73-75% and 91-92% of the critical stress intensity factor K_{IC} for Z 3 Y-I, and 69-70% and 86-88% for Z 3 Y-II, respectively. A σ_f-ΔT curve for a certain failure probability level F showed instantaneous decline at a critical temperature differential ΔT_c. High failure probability level F resulted in a high critical temperature diffrential ΔT_c. Estimated ΔT_c's are 310°, 360° and 400°C for $F = 0.2$, 0.5 and 0.9, respectively.*

[*Received August 15, 1985*]

Preparation and Several Properties of Ferroelectric Powder $Pb\{(Mg, Zn)_{1/3}Nb_{2/3}\}O_3$ (Part 1)

Substitutional Solid Solubility of ZnO for MgO in Perovskite Type Lead Magnesio-Niobate

Fumio IMOTO, Hiroshi TAKASE and Nobuo KIMURA

(Faculty of Engineering, Shizuoka University
3-5-1, Johoku, Hamamatsu-shi 432)

Powders containing perovskite type double oxides of the series $Pb(Mg_{1/3}Nb_{2/3})O_3$-$Pb(Zn_{1/3}Nb_{2/3})O_3$ as a main constituent have been prepared by firing the batch mixture according to the chemical formulae. It is interesting to know the substitutional solid solubility of ZnO for MgO in this series because the latter end member $Pb(Zn_{1/3}Nb_{2/3})O_3$ is known not to be prepared under ordinary firing conditions. The substituted ratio was estimated by the precise determination of lattice constant and its comparison with the Vegard's line. It was shown that MgO in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ was able to be substituted by ZnO up to 35 or 40 mol% depending on the firing temperature (950° or 1100°C). Peak temperature of capacitance (corresponding to Curie point) of the fired disc varied from 0° to 40°C depending on the substitutional ratio of this series. Parallelism between the observed data and the predicted line connecting the Curie points of the end members suggested that the substitution of ZnO for MgO proceeded up to 30-35 mol % in this series. However, a certain unbiguity still remained as the observed data at the higher substitutional ratios of the batch mixture were shown to be considerably high. Single crystals of this series were prepared by the "PbO-flux method". According to the variation of the lattice constant of perovskite type crystal along with the feed composition, it was judged that the homogeneous substitution of ZnO for MgO went up to 30-35 mol % in this series. Summarizing the above-mentioned results it has been concluded that the solid solubility of ZnO for MgO in this series is 35±5 mol %.

[*Received August 31, 1985*]

Thermal Conductivity of Reaction Bonded Si_3N_4

Kunio HAYASHI, Shinji TSUJIMOTO, Tomozo NISHIKAWA and Yasuo IMAMURA*

(Department of Chemistry, Kyoto Insutitute of Technology
Matsugasaki, Sakyo-ku, Kyoto-shi 606
* Denki Kagaku Kogyo Co., Ltd.)

To investigate the effect of α- and β-Si_3N_4 content on the thermal conductivity of silicon nitride ceramics, six samples containing various quantities of α-Si_3N_4 were prepared by the reaction bonding process and the thermal conductivity of the reaction bonded Si_3N_4 (RBSN) was measured by the transient hot wire method at various temperatures from room temperature to 1000°C. The RBSN samples containing 1, 25, 33, 45, 55 and 66% α-Si_3N_4 were produced by nitriding the compacts of pure silicon powder in a nitrogen atmosphere at 1480°C for prescribed periods. Bulk density, true density and total porosity of samples were 2.51±0.02 g/cm³, 3.08±0.03 g/cm³ and 18.6±1.0%, respectively, regardless of the α-content. No significant change in microstructure of RBSN samples was observed by scanning electron microscopy. With an increase in the content of α-Si_3N_4, the thermal conductivity (λ) of BRSN samples decreased from $\lambda = 17.4\ Wm^{-1}\ K^{-1}$ for the sample with α-Si_3N_4 of 1% (viz. consisted mainly of β-Si_3N_4) to $\lambda = 9.3\ Wm^{-1}\ K^{-1}$ for that of 66%. It was considered that the α-Si_3N_4 solid solutions by which the thermo-elastic wave carrying the heat energy in the non-electro-conductive solid materials such as Si_3N_4 ceramics is scattered, might be formed with the impurities included in silicon powder as a starting