

# Glass Properties in the Yttria-Alumina-Silica System

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*The glass formation region in the yttria-alumina-silica system was investigated. Properties of glasses containing 25 to 55 wt% yttria were measured and the effect of the composition was determined. The density, refractive index, thermal-expansion coefficient, and microhardness increased with increasing yttria content. The dissolution rate in 1N HCl increased with increasing yttria content and temperature. These glasses were also found to have high electrical resistivity.*

INTEREST in glass formation in the system  $Y_2O_3-Al_2O_3-SiO_2$  (YAS) stems from its intended use in making radiotherapeutic microspheres. In this application, a radioactive isotope is incorporated within a suitable carrier, and the carrier is injected into the target organ. The carrier must be chemically durable so that the isotope is not released in vitro. It should also have moderate density to allow it to be suspended in an injection medium.

The advantage of using YAS glass as the carrier is that the desired element is incorporated within the glass structure, and the isotope  $^{90}Y$  is activated in situ by neutron bombardment. In this way, handling of radioactive materials during the manufacturing process is avoided. The YAS glass also meets the requirement that the other constituents (Al, Si, O) are unaffected by the irradiation. Most oxide glasses have inherently high chemical durability, and their density can be adjusted by compositional variation.

Because of the scarcity of published data for the YAS glasses,<sup>1-3</sup> a study of their physical properties as a function of composition was conducted. A relatively large compositional region for glass formation is

present in the YAS system.<sup>1</sup> Ten YAS compositions, with yttria content varying from 25 to 55 wt%, were studied. Only glasses that melted below 1600°C were prepared. The chemical durability, density, thermal-expansion coefficient, softening and transformation temperatures, microhardness, refractive index, and dc electrical resistivity were measured.

## EXPERIMENTAL PROCEDURE

### Glass Preparation

The compositions listed in Table I were prepared from reagent-grade chemicals.<sup>4</sup> A homogeneous powder mixture weighing 25 or 50 g was melted in a platinum crucible in an electric furnace at 1500° to 1600°C. The melt was held at temperature for ≈3 h for fining and homogenization. The melt was cast into steel molds to form bars ≈1 by 1 by 6 cm, which were annealed at ≈800°C for 8 to 12 h and slowly cooled to room temperature. The glass remaining in the crucible was quenched in water, broken from the crucible, and saved for property measurements.

### Property Measurements

The density was measured by the Archimedeian method using water as the suspending medium. The thermal-expansion coefficient ( $\alpha$ ), softening temperature ( $T_s$ ), and transformation temperature ( $T_g$ ) were measured<sup>5</sup> with either 2.54- or 5.08-cm samples which were heated in air at 5°C/min.

The refractive index ( $n_D$ ) was mea-

sured by the Becke line technique using white light. The Abbe number ( $\nu$ ) or reciprocal relative dispersion was measured for YAS-4.

Filters<sup>6</sup> were placed in front of a white light source which transmitted light at 488.4, 588.9, and 656.2 nm. The index measured at 488.4 and 656.2 nm was converted to the index at the F (486.1 nm) and C (656.3 nm) Fraunhofer lines, respectively, using calibration data provided with the refractive index liquids.<sup>7</sup> The index measured at 588.9 nm corresponds to the index for the sodium D line. The Abbe number was calculated from the equation

$$\nu = (n_D - 1) / (n_F - n_C) \quad (1)$$

where  $n_F - n_C$  is the partial dispersion.

A hardness tester\*\* with a diamond indenter was used to measure the Vickers hardness number (VHN). A load of 100 g was applied for 30 s to a glass sample whose surface had been polished with 1- $\mu$ m alumina. At least five indentations were made on each sample, with the average length of the indentation diagonals used to calculate the VHN. The VHN in gigapascals was calculated from the equation

$$VHN = (18.19P) / d^2 \quad (2)$$

where  $P$  is the load in grams and  $d$  is the average diagonal length in micrometers.

The infrared (IR) spectra<sup>††</sup> of YAS-2, -4, -5, -7, and -8 and crystalline  $Y_2O_3$  were measured from 4000 to 200  $cm^{-1}$ . The IR spectra of devitrified YAS-2 and -7, heated at 1100°C for 6 h, were also measured. The IR spectra were measured using pellets prepared by mixing 1 mg of powdered sample with 300 mg of KBr and pressing at 138 MPa.

The dc electrical resistivity of YAS-4 and -7 was measured from 200° to 400°C at 25°C intervals. Samples measuring ≈0.1 by 1 by 1 cm were cut from glass bars, and gold electrodes were evaporated onto the 1 by 1 cm surfaces. The sample was heated in a dry nitrogen atmosphere in a closed tube furnace. After the desired temperature was reached, the sample was equilibrated for ≈5 min, then a dc field of ≈240 kV/m was applied, and the steady-state current was measured with an electrometer.<sup>‡‡</sup>

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Table I. Characteristics of the Glass Compositions Investigated

Glass	Batch composition (wt%)			$T_g$ (°C)	$T_s$ (°C)*	$\alpha \times 10^7$ (°C <sup>-1</sup> ) <sup>‡</sup>
	$Y_2O_3$	$Al_2O_3$	$SiO_2$			
YAS-5	25	20	55	890	947	31
YAS-1	33	21	46	889	933	39
YAS-4	40	20	40	884	934	51
YAS-3	50	20	30	892	937	62
YAS-2	55	20	25	886	935	70
YAS-9	55	15	30	895	936	57
YAS-7	40	30	30	885	941	50
YAS-10	35	35	30	884	935	48
YAS-6	42	25	33	884	934	53
YAS-8	40	13	47	892	943	47

\*±5°C. †100–700°C.

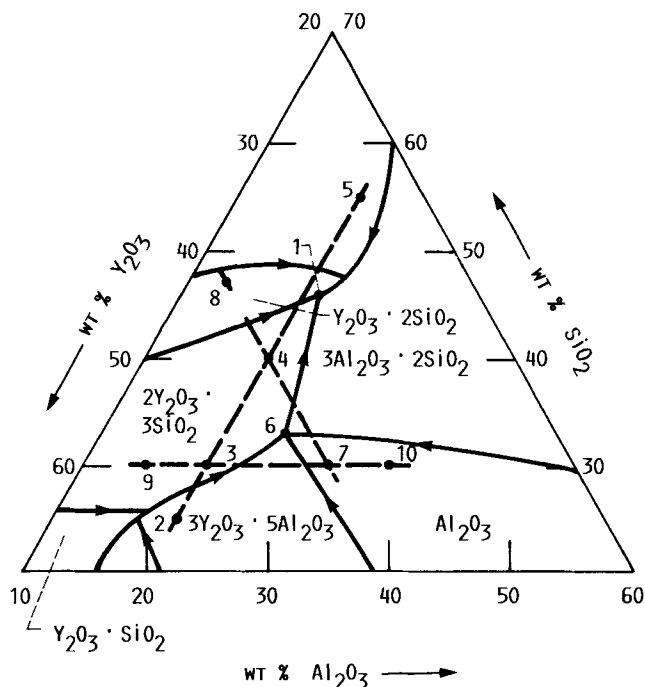


Fig. 1. Diagram of the system  $Y_2O_3$ - $Al_2O_3$ - $SiO_2$  where the numbers 1 through 10 show the compositions of the glasses investigated.

The data were fitted to an Arrhenius equation

$$\log \rho = \log \rho_0 + \frac{Q}{2.3026RT} \quad (3)$$

where  $\rho$  is the resistivity,  $\rho_0$  is the pre-exponential term,  $Q$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature. The equation was then used to calculate the Arrhenius parameters for the electrical resistivity of YAS-4 and -7.

#### Chemical Durability Measurements

A preliminary measurement of the chemical durability was made by placing weighed amounts of YAS glass powder (particle size  $-74$  to  $+44 \mu m$ ) in plastic bottles containing 50 mL of distilled water. These bottles were placed in a constant-temperature water bath and gently agitated for 15 d. The percent weight loss was calculated for each sample.

The dissolution rate of YAS glasses was also determined in 1N HCl at 30° and 50°C. One group of samples consisting of YAS-2, -3, -5, -6, -7, -8, and -9 was tested at 50°C for 7 d. A second group consisting of YAS-4, -7, -8, and a control sample of fused  $SiO_2$  was tested at 30°C for 15 d.

Rectangular samples  $\approx 0.5$  by 0.75 by 1 cm were cut and weighed, and their exact dimensions measured before being placed in high-density polyethylene bottles containing 50 mL of 1N HCl. The bottles were placed in a constant-temperature water bath and gently agitated. The weight change of each sample was measured periodically by removing the sample from the bottle, rinsing it in distilled water, drying with hot air, and weighing it. Measurements at 50°C were made after 1 and 7 d. Measurements at 30°C were made at 3-d intervals up to 15 d.

The dissolution rates ( $DR$ ) were calculated by the equation

$$DR = \frac{dw}{At} \quad (4)$$

where  $dw$  is the weight loss for the sample between each time period,  $A$  is the sample surface area, and  $t$  is the time between measurements.

## RESULTS AND DISCUSSION

### Glass Melting

The 10 glass compositions prepared are shown on the YAS phase diagram in Fig. 1 and are given in Table I. Seven of the glasses were transparent with a slight yellow tint. Of the remaining three, YAS-5 and -8 were phase-separated, and YAS-2 was partly crystallized.

YAS-8 was milky white and opaque throughout the bulk of the material. YAS-5 was slightly cloudy, but partly transparent. Figure 2 shows the appearance of the acid-etched fracture surfaces of YAS-5 and -8. The photographs seem to indicate that YAS-5 is more phase-separated than YAS-8, but the visual appearance of the samples suggests the opposite.

X-ray diffraction (XRD) analysis confirmed the partial crystallinity of YAS-2. The crystallinity in YAS-2 might be eliminated by melting above 1600°C, but this was the maximum temperature available in the present work.

Of the 10 compositions investigated, YAS-5 and -8 are positioned closest to a two-liquid region in the  $Y_2O_3$ - $SiO_2$  system which extends out into the YAS system.<sup>4</sup> YAS-5 and -8 would be the most likely compositions to show phase separation.

### Properties

**Density.** The density of the YAS glasses varied from 3.81 to 2.86 g/cm<sup>3</sup>. As illustrated in Fig. 3, the greatest change in density occurs when  $SiO_2$  or  $Al_2O_3$  is substituted for  $Y_2O_3$  because of the large difference in molecular weight between  $Y_2O_3$ ,  $SiO_2$ , and  $Al_2O_3$ . There is good agreement between the densities measured in the present work and those reported pre-

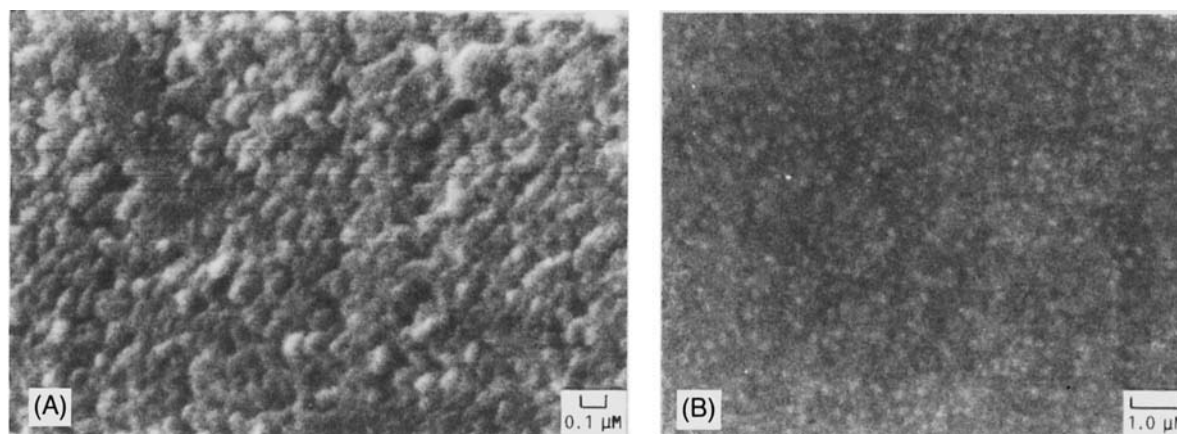


Fig. 2. Fracture surfaces of YAS glasses after a 5-s etch with HF: (A) YAS-5 and (B) YAS-8.

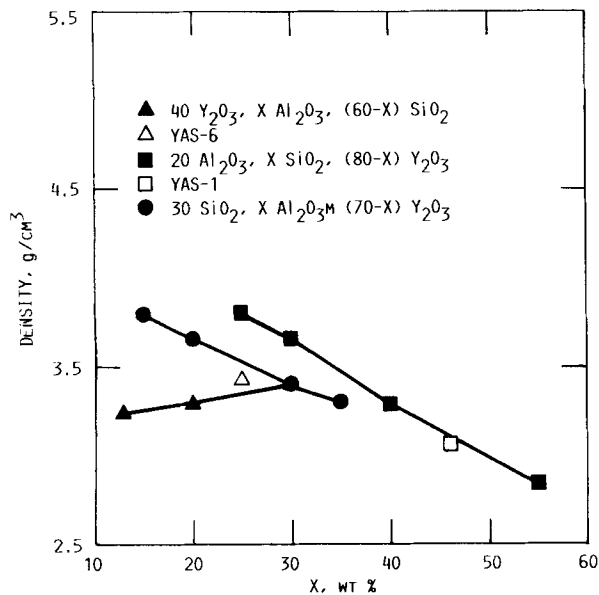


Fig. 3. Density vs composition for YAS glasses. Estimated error in density is  $\pm 0.05$ .

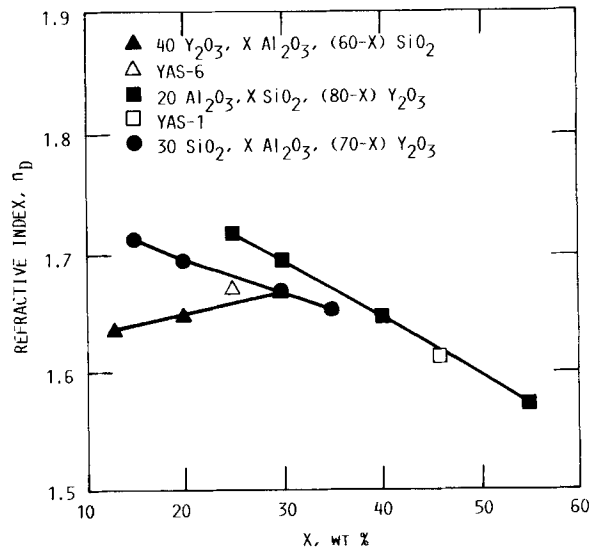


Fig. 4. Index of refraction vs composition for YAS glasses. Estimated error in refractive index is  $\pm 0.004$ .

viously.<sup>3</sup> Overall, the density of the glass is a function mainly of the molecular weights of the oxides in the glass.

**Thermal Expansion.** Table I gives the softening temperature, glass transition temperature, and average thermal-expansion coefficient (from  $\approx 100^\circ$  to  $700^\circ\text{C}$ ) of the YAS glasses studied. The  $T_s$  and  $T_g$  values show that these glasses are refractory, and  $T_s$  varies only slightly with composition. Generally, the expansion coefficient increases with increasing  $\text{Y}_2\text{O}_3$  content and decreases as  $\text{SiO}_2$  is added.

**Refractive Index.** The refractive index of the YAS glasses varied from 1.717 to 1.572, as shown in Fig. 4. The refractive index tends to increase with increasing  $\text{Y}_2\text{O}_3$  content. The greatest decrease in index occurs when  $\text{SiO}_2$  is substituted for  $\text{Y}_2\text{O}_3$  while keeping the  $\text{Al}_2\text{O}_3$  content constant. The Abbe number of YAS-4 ( $n_F=1.654$  and  $n_C=1.639$ ) was 43.0, with a partial dispersion of 0.015. These values for this glass fall within the range of commercial optical glasses.<sup>5</sup> As expected, the change in refractive index with composition (Fig. 4) followed the same pattern as the density (Fig. 3). Increasing the yttria content increased the density and packing factor of the glass, thereby increasing its ability to refract light. There is good agreement between the refractive index values reported<sup>1-3</sup> previously and those of the YAS glasses in the present work.

**Vickers Hardness Number (VHN).** The VHN of the YAS glasses varied from 6.36 to 8.28 GPa, as shown in Fig. 5. The  $\text{Y}_2\text{O}_3$  content had a large effect on the VHN, and glasses of high  $\text{Y}_2\text{O}_3$  content were harder. The VHN of the YAS glasses in the present work are comparable to those reported previously.<sup>2,3</sup> A VHN of 9.80 GPa has been reported<sup>2</sup> for a 63.8 wt%  $\text{Y}_2\text{O}_3$ , 5.5 wt%  $\text{Al}_2\text{O}_3$ ,

30.7 wt%  $\text{SiO}_2$  glass. The VHN for these glasses is high compared to other glasses. For example,<sup>6</sup> fused silica has a VHN of  $\approx 5.9$  GPa. The variation in VHN with composition follows the same trend as the density and refractive index.

**IR and XRD.** The structure of YAS glass is apparently a continuous, closed network. The IR spectra of all glasses measured were similar. Figure 6 shows the IR spectra for samples of YAS-2, -4, and -7 glasses along with the spectra for devitrified samples YAS-2D and -7D. The absorptions at  $1120$  and  $480\text{ cm}^{-1}$  indicate the presence of  $\text{SiO}_4$  and  $\text{AlO}_6$  groups in the glass.<sup>7,8</sup> The wide band centered at  $950\text{ cm}^{-1}$  is probably due to yttrium groups in the glass, but the coordination of yttrium in these glasses is uncertain. The IR spectra of the devitrified samples were similar to those of the glass. The only difference was

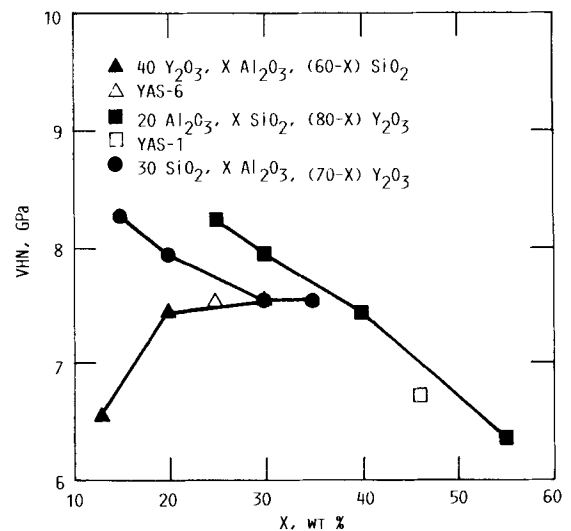


Fig. 5. Vickers hardness number vs composition for YAS glasses. Estimated error in VHN is  $\pm 0.5$ .

the addition of sharp peaks on the transmittance curve which are attributed to the crystalline nature of the samples.

Analysis by XRD of devitrified YAS-2 showed it contained  $\text{Y}_2\text{O}_3:\text{SiO}_2$  and  $3\text{Y}_2\text{O}_3:5\text{Al}_2\text{O}_3$ . The compounds  $3\text{Y}_2\text{O}_3:5\text{Al}_2\text{O}_3$  and  $2\text{Y}_2\text{O}_3:3\text{SiO}_2$  are the major devitrification products expected on the basis of the YAS phase diagram<sup>4</sup> but the latter was not identifiable in the XRD pattern.

Analysis by XRD of devitrified YAS-7 showed it contained mullite ( $3\text{Al}_2\text{O}_3:2\text{SiO}_2$ ) and  $\text{Y}_2\text{O}_3:2\text{SiO}_2$ . Based on the published phase diagram,<sup>4</sup> alumina and mullite are the major devitrification products expected, but there was no evidence of alumina in the XRD pattern.

**Direct Current Electrical Resistivity.** The change in the dc resistivity of YAS-4 and -7 with temperature is shown in Fig. 7.

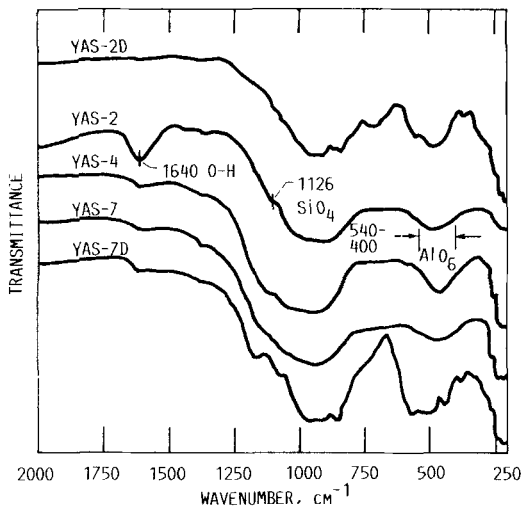


Fig. 6. Infrared spectra of vitreous and devitrified YAS composition.

Table II. Arrhenius Parameter Values for the Direct Current Electrical Resistivity of  $Y_2O_3-Al_2O_3-SiO_2$  Glasses

Glass	Temperature range (°C)	$(DR) \times 10^7$ (g/(cm <sup>2</sup> ·min))	
		0 to 6 d at 30°C	0 to 15 d at 30°C
YAS-4	200-400	110.3	1.47
YAS-7	200-400	128.7	-2.45

The Arrhenius parameters calculated for YAS-4 and -7 are given in Table II. The two glasses measured have roughly equal resistivities; YAS-7 has a higher activation energy than YAS-4. Any conductivity in the glass must be attributed to the presence of impurities in the sample which act as charge carriers.

<sup>88</sup>Pyrex, Corning Glass Works, Corning, NY.

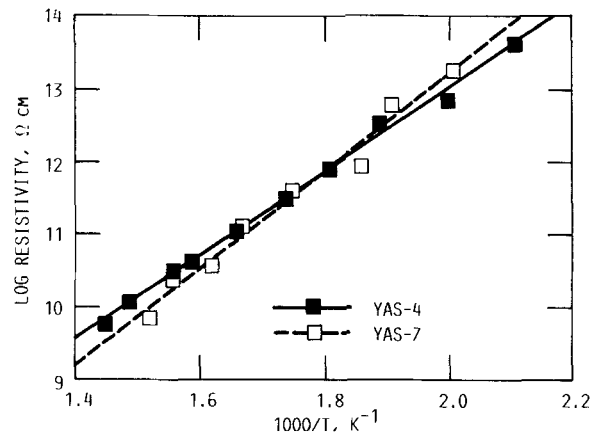


Fig. 7. Direct current electrical resistivity vs temperature for YAS-4 and -7.

Table III. Dissolution Rates (DR) of YAS Glasses and Vitreous Silica in 1N HCl (Solution pH=1.0)

Glass	$(DR) \times 10^7$ (g/(cm <sup>2</sup> ·min))		
	0 to 6 d at 30°C	0 to 15 d at 30°C	0 to 7 d at 50°C
YAS-2			54.6
YAS-3			36.2
YAS-4	2.8	2.1	7.8
YAS-5			3.4
YAS-6			28.1
YAS-7	5.7	6.8	28.3
YAS-8	3.9	2.8	7.2
SiO <sub>2</sub> <sup>*</sup>	0.5	0.055	

\*Rod-shaped sample.

#### Chemical Dissolution

The data in Table III show that the glasses of higher  $Y_2O_3$  content had higher dissolution rates in 1N HCl. Overall, the YAS glasses had a higher dissolution rate in 1N HCl than fused silica. In alkaline solutions the durability of YAS glass is significantly higher<sup>9</sup> than that of silica or borosilicate glass.<sup>88</sup> In glasses of constant

$Y_2O_3$  content, the solubility increased as the  $Al_2O_3$  content increased. The solubility also increased with temperature, as expected.

The change in dissolution rate of the glasses in 1N HCl at 30°C followed a uniform pattern. The dissolution rate decreased during the first 6 d, then became fairly constant for the remainder of the test.

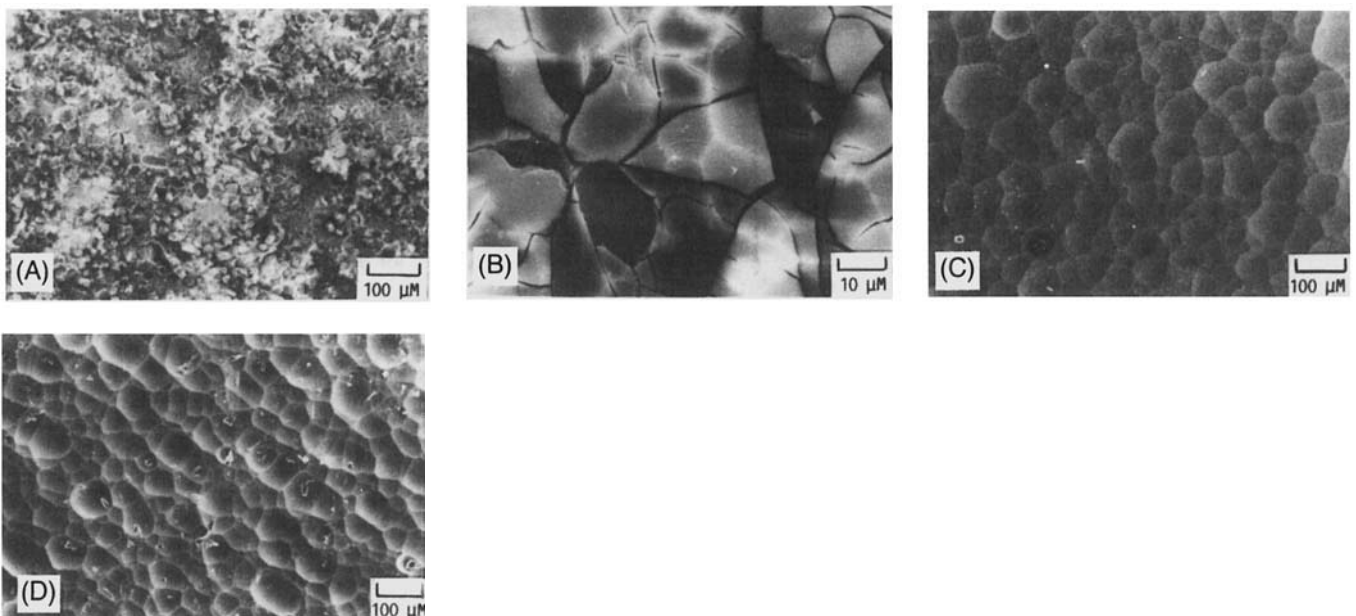


Fig. 8. Appearance of the external surface of YAS glasses placed in 1N HCl. (A) and (B) YAS-4 after 15 d at 30°C, (C) YAS-2 after 7 d at 50°C, and (D) YAS-6 after 7 d at 50°C.

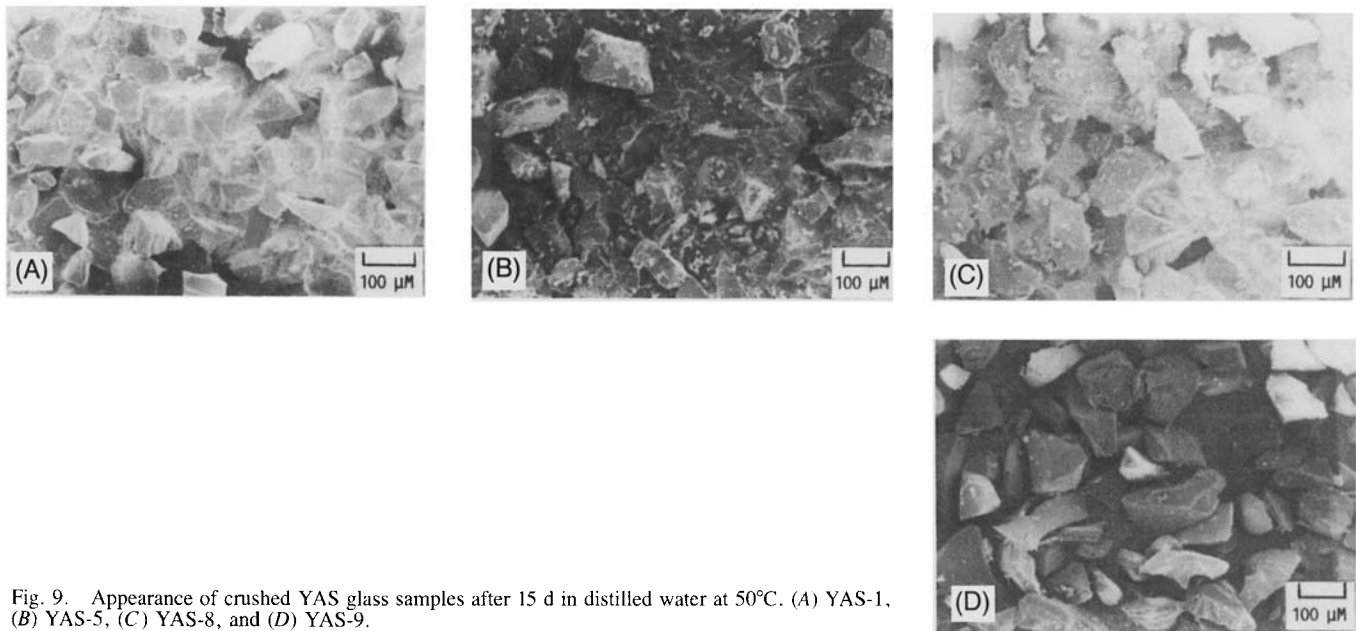


Fig. 9. Appearance of crushed YAS glass samples after 15 d in distilled water at 50°C. (A) YAS-1, (B) YAS-5, (C) YAS-8, and (D) YAS-9.

The continuous weight loss of the samples suggests that corrosion occurs by dissolution of the glass network.

As shown in Fig. 8, there is a noticeable amount of chemical attack for each glass sample placed in 1N HCl. The degree of attack on the surface of the YAS-4 glass is evident by the large fissures on the surface, shown in Figs. 8(A) and (B). A texture resembling grain structure often appeared during the durability test, as shown by the YAS-2 and -6 glasses.

As shown in Fig. 9, YAS glass placed in distilled water showed little evidence of corrosion. No etching or pitting occurred, and the sharp edges of the fragments are still present.

#### CONCLUSIONS

The density, refractive index, microhardness, and thermal expansion of YAS glasses vary significantly with the  $Y_2O_3$

content. The YAS glasses exhibit higher density, refractive index, and microhardness than does fused silica. The YAS glasses are refractory, with a  $T_g$  value varying from  $\approx 800^\circ$  to  $900^\circ C$ , depending on composition. This transformation temperature is not quite as high as that of fused silica, but YAS glasses are more easily melted and prepared. The YAS glasses also have high thermal expansion compared to their high  $T_g$ . Normally, the expansion coefficient will decrease as  $T_g$  increases. The high microhardness values found for YAS glasses indicate that they should have good abrasion resistance. The YAS glasses tested have a high dc electrical resistivity, with activation energies of 110 and 129 kJ/mol. The chemical durability of YAS glass in distilled water is very high. In 1N HCl, the dissolution rates of YAS glasses are low, but much higher than that of fused silica. Also, the dissolution rates increase with temperature and  $Y_2O_3$  content.

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