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PROPERTY SURVEY OF Y_2O_3-Al_2O_3-SiO_2-M_xO_y GLASSES

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AMY LEE APPLEWHITE, 1962-

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Approved by

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ABSTRACT

The purpose of this work was to investigate the properties of Y_2O_3-Al_2O_3-SiO_2-M_xO_y glasses. Many M_xO_y components were tested, but TiO_2 and B_2O_3 proved the most interesting. Glasses containing 5 to 25 wt % TiO_2 were melted and found to have improved chemical durability and a higher refractive index and density than the eutectic Y_2O_3-Al_2O_3-SiO_2 starting glass. These glasses could be crystallized to form an opaque glass ceramic. Glasses containing B_2O_3 were formed by exchanging SiO_2 with B_2O_3 while holding the Y_2O_3 and Al_2O_3 content constant. The density, hardness, refractive index, transformation temperature, softening temperature and chemical durability decreased with increasing B_2O_3 content, while the thermal expansion coefficient increased.

I. INTRODUCTION

A previous study[1] determined Y_2O_3-Al_2O_3-SiO_2 (YAS) glasses to be useful in delivering therapeutic radiation to liver cancer patients. Microspheres of YAS glass were bombarded by neutrons, forming radioactive Y-90, an isotope suitable for radiation therapy. A suspension of these radioactive microspheres could be injected into the hepatic artery and, after lodging in the liver, could deliver a therapeutic dose of radiation to cancerous liver tissue.[1] This discovery created an interest in YAS glasses.

A large compositional range for glass formation is known to exist,[2] but not all possible applications have been studied. YAS glasses are known to be chemically durable and to have a relatively high refractive index, hardness, and softening temperature.[1]

An investigation of the Y_2O_3-Al_2O_3-SiO_2-M_xO_y (YASM) system was undertaken. It was decided that a general property survey would be a valuable endeavor as little is known about this system. It was hoped that a specific beneficial property could be enhanced by adding an additional oxide to a the YAS base glass composition. YASM glasses have been prepared with La_2O_3, TiO_2, P_2O_5 and ZnO,[3-6] but a general property survey has not been made. La_2O_3 and TiO_2 additions increase the refractive index, hardness, elastic modulus and alkaline durability.[3-4] ZnO causes a curious convex pyramidal crystallization on the surface of the glass.[5] P_2O_5 was found to form a fully crystalline glass ceramic.[6] These results were interesting, but did not completely demonstrate the potential usefulness of these glasses

The eutectic YAS composition ($42Y_2O_3$-$25Al_2O_3$-$33SiO_2$ wt %) was chosen as the starting glass. Ten weight % of various metal oxides were added to the YAS starting composition. The plan was to survey the properties of many glasses and to study any that demonstrated interesting properties in more detail.

The first criteria for further study was whether the melt formed a glass. If glass was formed, preliminary measurements were made including: refractive index, density and micro-hardness. For compositions that showed promise, thermal expansion coefficient, transformation and softening temperatures, acid durability, radio-opacity and devitrification behavior were also investigated.

Two families of glasses proved to be most interesting: YAST ($T=TiO_2$) and YASB ($B=B_2O_3$). The YAST glasses could be crystallized to form an opaque, chemically durable glass ceramic. YAB glasses, Y_2O_3-Al_2O_3-B_2O_3 have been investigated previously[7] so the YASB glasses, $20Y_2O_3 \cdot 25Al_2O_3 \cdot (55-x)SiO_2 \cdot xB_2O_3$, allowed a means of direct comparison between YAS and YAB glasses.

II. EXPERIMENTAL PROCEDURE

A. GLASS PREPARATION

Reagent grade chemicals[*] were weighed[**] and mixed. Fifty gram batches were melted in platinum crucibles at 1400-1600°C for three hours in a bottom loading electric furnace.[+] The melts were stirred periodically with a fused silica rod to improve homogeneity. The melts were cast into steel molds to form bars measuring ≈ 1 x 1 x 8 cm. These bars were quickly placed in an annealing furnace at ≈800°C. After allowing about 30 minutes for the bars to thermally equilibrate, the furnace was shut off and the bars left to cool slowly overnight.

B. PROPERTY MEASUREMENTS

The refractive index was measured on small glass fragments by the Becke line method. Calibrated refractive index liquids,[++] and a white light filter,[#] which permitted the transmission of only sodium D light, were used.

The density was measured by the Archimedian method (ASTM C20-80a) using kerosene as the suspending medium. Three specimens of each glass were measured. The density was calculated from

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$$B = \frac{D}{D - S} \times P \qquad (1)$$

where B is the bulk density, D the dry weight, S the suspended weight and P the density of the suspending medium. The three density values were averaged to obtain the value reported herein.

The Vickers Hardness Number (VHN) was measured with a microhardness tester[*] equipped with a diamond indenter. A load of 83.3 g was applied for 10 s to a glass block that had been polished with one micron alumina powder. Seven pyramidal indentions were made on each sample. The VHN was calculated (in GPa) from

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

where P is the load in grams and d is the average diagonal length of the pyramid base in micrometers.

The thermal expansion coefficient (α), transformation temperature (T_g), and softening temperature (T_s) were measured with an automatic recording dilatometer.[**] One inch samples were heated in air at 5°C/min. The slope of the graph of Δlength versus temperature gave $_0$, the temperature at which the changing slopes intersected was used to estimate T_g, and the temperature where the curve peaked gave T_s.

The infrared, IR, spectrum[+] of each YASB glass was measured

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[*] Microhardness Tester, C. Reichert Optische Werke, Vienna, Austria.
[**] Automatic Recording Dilatometer, The Edward Orton, Jr. Ceramic Foundation, Westerville, OH, USA.
[+] 599 Infrared Spectrophotometer, The Perkin-Elmer Corporation, Norwalk, CT, USA.

from 4000 to 200 cm^{-1} using pellets pressed from a mixture of 300 mg of potassium bromide and 1.8 mg powdered glass. The pellets were pressed in a vacuum die at ≈678 MPa.

Solid state nuclear magnetic resonance (NMR) techniques were used to characterize the ^{29}Si and ^{27}Al in the YASB glasses. Magic angle spinning (MAS) was used to eliminate line-broadening interactions. The spectrometer frequency of ^{29}Al and ^{27}Si is 52.11 and 39.73 MHz, respectively. The glasses, studied as fine powders, were prepared manually with an alumina mortar and pestle.

C. GRADIENT DEVITRIFICATION

Preliminary tests indicated that YAST glasses could be converted to a glass ceramic by heating above the temperature where they crystallized. To better evaluate this behavior, a gradient devitrification profile was performed. Small blocks of YAST-20 (20 weight % TiO_2) glass were placed at one inch intervals on a refractory setter covered with alumina particles. The setter was inserted into an electrically heated tube furnace after the temperature inside the furnace tube had been measured at one inch intervals. The thermal treatment of each specimen was controlled by positioning it in the furnace at the desired temperature. The samples were held between 771° and 1051°C for two hours. The extent of devitrification was determined by visual examination and from density measurements.

D. RADIO-OPAQUE IMAGE DENSITY

A potentially useful property of YAS glasses is their radio-opacity; i.e. they are highly absorbing to X-rays. A

radiographic inspection unit[*] was used to make radiographs of various specimens. The X-ray film was shielded by lead screens to reduce scatter of the x-rays and to produce a sharper picture. Tungsten white radiation of a continuous spectrum was the x-ray source. An aluminum wedge with 10 machined 0.08 cm steps was the standard. The image density of the radiographs was measured with a densitometer,[**] an instrument which measures relative brightness intensity of radiographic images.

E. GLASS-POLYMER COMPOSITE PREPARATION

A possible application of radio-opaque glasses is as a filler in dental restorative materials.[8] Glass fillers are added to a polymer to form a composite material suitable for filling caries in teeth. The glass filler reduces the shrinkage of the composite and improves the chemical durability, strength and translucence of the restoration. Specimens were fabricated to compare their relative radio-opacity with that of existing restorative composites.

Polymethylmethacrylate (PMMA) and YAS or YAST(20)D (D means devitrified) powders were mixed and placed in resilient plastic containers that could be heat sealed to specific dimensions. Specimens were prepared in two ways: in the first instance the PMMA was partially gelled and the powder massaged throughout to form an approximately homogeneous mixture; in the second instance

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[*] FAXITRON Radiographic Inspection Unit, Field Emission Corporation, McMinnville, OR, USA.
[**] Kodak Color Densitometer, Model 1, Eastman Kodak Company, Rochester, NY, USA.

the glass powder was allowed to settle in the PMMA which then hardened to form a dense, uniform mixture.

F. CHEMICAL DURABILITY

The dissolution rates of YAST, YAST-D and YASB specimens were determined in pH=1 HCl. Wafers of glass were sliced from the annealed bars. The dimensions of each wafer were measured and used to calculate its surface area. The wafers were placed individually into bottles filled with the HCl solution and kept at a constant 30°C. Periodically, each wafer was removed, washed, dried and weighed. The weight loss in mg/cm^2 was calculated from

$$\text{weight loss} = \frac{\text{change in weight}}{\text{surface area}} \quad (3)$$

Similarly, the dissolution rate, DR, was calculated from

$$DR = dw/At \quad (4)$$

where dw is the cumulative weight change of the specimen, A is the sample surface area and t is the elapsed time for each measurement.

III. RESULTS AND DISCUSSION

A. PRELIMINARY MEASUREMENTS

1. Glass Formation

The eutectic YAS composition ($42Y_2O_3$-$25Al_2O_3$-$33SiO_2$ wt %)
was the starting basis for all the compositions melted.
Initially additions were made to the base glass in 10 wt %
increments.

In some instances, see Table I, the compositions did not
melt below $1600^\circ C$ which was the maximum usable temperature for
the glass melting furnace. The YAS-P(10) composition melted only
partially and formed a substance too viscous to cast. The
YAS-Zr(10) composition was an inhomogeneous, glassy solid that
contained undissolved particles.

If a transparent, homogeneous glass resulted when 10 wt %
of M_xO_y was added to the YAS glass, the amount of M_xO_y was
increased in 5 wt % increments until glass formation disappeared.
The initial compositions containing ZnO, BaO, SnO_2 and TiO_2 formed
glass. However, only TiO_2 formed a transparent glass above 10
wt %. In fact, some glass formation persisted in compositions
containing up to 25 wt % TiO_2.

2. Refractive Index

The refractive index, RI, of the YAS eutectic composition
was 1.65 which agrees with that reported previously.[1] Two factors
should be taken into account when determining the change in
refractive index: the amount and the size of atoms added to the

starting glass. The addition of larger atoms increases the packing factor or density of the glass which also increases its refractive index.

The compositions melted were prepared in wt % which causes the number of atoms added to each different composition to vary. This made it difficult to directly compare RI values. However, as may be seen in Table I, the refractive index increased whenever the atomic number of the cation in the M_xO_y addition exceeded than that of Si.

The YAS-Pb(10) glass had the highest RI at 1.707. YAS-Sn(10) and YAS-Zn(10) glasses also had high values of RI: 1.678 and 1.675, respectively. YAS-B(10), B having a lower atomic number than Si, had the lowest RI at 1.643.

3. Vickers Microhardness

The YAS starting glass had a VHN of 6.85 GPa, higher than all the other glasses initially investigated. As can be seen in Table I, the YAS-Zn(10) glass had the next highest VHN at 6.64 GPa. The YAS-Ba(10) glass had the lowest VHN at 6.17 GPa. The VHN of all the glasses containing 10 wt % of M_xO_y was lower than that of the YAS starting glass.

A high Y_2O_3 content has been linked to high hardness values in the past.[1] The YAS starting glass had a higher Y_2O_3 content than those having M_xO_y additions, which can account for its higher hardness.

4. Density

As may be seen in Table I, the density increased with M_xO_y additions ranging from 3.45 g/cm^3 for YAS to 3.767 g/cm^3 for the

YAS-Pb(10) glass. There is good agreement between the densities measured in this study and those reported previously for YAS, YAS-Ti and YAS-Zn.[1,3,4] The increase in density is attributed to the higher molecular weight of the M_xO_y additions. Density is primarily a function of the molecular weight of the constituent oxides of a glass.

B. YAST COMPOSITIONS

Glass was formed when up to 20 wt % TiO_2 was added to the YAS base glass. TiO_2 caused a brown tint to the glass, progressing from amber at 5 wt% to dark brown at 20 wt % TiO_2. Brown glassy stria were evident in YAS-Ti(25), a composition that yielded an otherwise white, opaque material when cast. Density, refractive index and VHN all increased with increasing TiO_2 content because of the increased size and molecular weight of the titanium atoms.

YAST glasses formed glass ceramics when heated above their annealing temperatures. The TiO_2 acted as a nucleating agent for crystallization. The resulting glass ceramic was pale gray and completely opaque. Tests showed it to be chemically durable, hard and dense.

1. Devitrification

To determine the conditions necessary to promote devitrification, identical specimens of YAST(20) glass were heated at various temperatures. Fig. 1 shows the change in appearance of the YAST(20) specimens after two hours at temperatures from $771^{\circ}C$ to $1051^{\circ}C$. The YAST(20) glass contained colored striations. The darker stria, which were the first to devitrify, were probably

TiO_2 rich regions. Devitrification did not begin until 840°C, at which point the crystalline regions became visible as milky swirls within the otherwise brown specimen. This devitrification pattern is also visible in the specimens in Fig. 1 heated at 894°C and 896°C. Close examination of the specimens showed some slight brown coloration remained until 955°C.

Fig. 2 shows the change in density that occurs at various stages of devitrification. As shown in Fig. 2, the density stayed constant until $\approx900^{\circ}$C where it sharply increased and became constant again when devitrification was complete.

The density of a glass ceramic is an additive function of the density of the glass and crystalline phases within it.[9] Crystals are ordered, making them denser than their amorphous counterparts (e.g. the density of fused quartz and cristobalite, is 2.21 and 2.32 g/cm^3 respectively).[10,11] X-ray diffraction* (XRD) analysis revealed $Y_2Ti_2O_7$, whose density is 4.987 g/cm^3 [12] to be the predominant crystalline component of the glass ceramic. The density of YAST(20)D was 3.81 g/cm^3. TiO_2, Y_2O_3 and Ti_3O_5 were also identified by XRD,[12] as crystalline components of YAST(20)D.

Crystalline SiO_2 and Al_2O_3 were not identified in the YAST(20)D sample which suggests they may have been present as an aluminosilicate glass.

2. Chemical Durability

Chemical durability was measured by monitoring the weight

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* Scintag PAD5, Scintag Scientific Computer and Instruments, USA.

loss of YAST specimens immersed in a pH=1 HCl solution. The test results are plotted in Fig. 3. The weight loss followed a uniform pattern, being higher initially and then becoming fairly constant after ≈3 days. The continuous weight loss indicates that corrosion occurred by uniform dissolution of the glass.

Additions of TiO_2 improved the chemical durability of the YAS glass. Fig. 3 shows that the durability of the YAST glasses increased with increasing TiO_2 content. Weight loss and dissolution rate are listed in Appendix A. The YAS glass lost 9.67×10^{-3} g/cm^2 after ≈5 days. YAST(20) lost less than 1.0×10^{-5} g/cm^2 over the same time period. Fig. 4 shows that the durability of YAST increased further when the glass was devitrified. YAST(25)D lost less than 1.0×10^{-6} g/cm^2 after ≈1 week in the HCl solution.

TiO_2 increases the chemical durability of the YAB glass for several reasons. TiO_2 is a durable oxide and Ti^{+4} fits very tightly within the glass network. The high charge of Ti^{+4} creates affinity toward the available O^{-2} ions within the glass network, and prevents leaching into corrosive environments. Crystallization increases the chemical durability further by producing very durable crystalline phases within an aluminosilicate glass network.

The improved chemical durability of YAS glass that results with TiO_2 additions is a very desirable property. High chemical durability is important for radiotherapeutic microspheres that will be exposed to the corrosive environment of the human body. Most importantly, TiO_2 does not form a harmful radioactive isotope

when subjected to neutron bombardment.[1]

3. Vickers Microhardness

The VHN of the YAS glass decreased from 6.85 GPa to 6.75 GPa with the addition of TiO_2. As more TiO_2 was added, the VHN began to increase until, at YAST(20) it was essentially the same as the original YAS composition, 6.84 GPa. The VHN increased after devitrification, reaching 8.28 GPa for YAST(25)D. Table II contains the data for the glass and crystallized YAST compositions.

C. YAS and YAST GLASS FILLED COMPOSITES

YAS glasses are radio-opaque which makes them a candidate for use in composite dental restorations. Bis-GMA is typically the polymer used commercially, as it can be cured in minutes with a UV light.[8] PMMA was used in this work to model the radio-opacity of a YAS/polymer composite.

Powdered YAS glass or YAST(20)D were mixed with PMMA, to make two types of samples. One sample contained ≈35 wt % glass powder, but was not homogeneously mixed, (unmix). The other sample was fabricated with a minimum of PMMA, and contained ≈85 wt % glass powder causing it to be homogeneous and dense, (dense).

Radiographs were made of these samples, as well as of a commercially prepared Bis-GMA composite[*] and liner cement[**]. Wafers of pure PMMA, YAS glass, YAST(20)D and a standard aluminum

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[*]   Chameleon light cure composite, shade: brown vita. St. Joseph, MO.

[**]   GC lining cement, glass ionomer cement for lining. GC Dental Industrial Corp. Tokyo, Japan.

step wedge were also tested. Fig. 5 shows the relative image density vs. sample thickness of these specimens.

Radio-opacity is a necessary property of dental restorations, it allows monitoring of filling integrity by x-ray pictures. A more radio-opaque filling is an improved filling. The values of the prepared samples are shown by individual points in Fig. 5. The aluminum standard, measured at varying thicknesses, is the solid line. The samples having the lowest image density are the most radio-opaque. As shown in Fig. 5, the dense composites containing YAS glass or YAST(20)D, along with the YAS glass and YAST(20) standards, are the most radio-opaque. The commercial Bis-GMA and liner cement and disperse (unmix) YAS+PMMA and YAST+PMMA samples are grouped just below the line for aluminum, indicating that they are all slightly more opaque than aluminum. The PMMA standard was virtually transparent to x-rays having an image density much higher than all the other samples.

D. YASB GLASSES

The YASB glasses were formed by substituting B_2O_3 for SiO_2 while holding the Al_2O_3 and Y_2O_3 content constant, i.e. YASB = $20Y_2O_3 \cdot 25Al_2O_3 \cdot (55-x)SiO_2 \cdot xB_2O_3$, mol %. These compositions were chosen to allow a comparison between YAS and YAB systems.[1,7] YASB, x=0, is the YAS-6 composition[1] modified to mole %, as indicated by an asterisk, i.e. YAS-6*.

1. Thermal Properties

Increasing B_2O_3 content lowered the transformation and softening temperatures, and increased the thermal expansion coefficient, as shown in Figs. 6 and 7, respectively. This is

expected, as B_2O_3 is more expansive and lower melting than SiO_2. The thermal expansion coefficient increases linearly from a low of 60×10^{-7} $^{\circ}C^{-1}$, for YAS-6*, to a high of 72×10^{-7} $^{\circ}C^{-1}$ for YAB-E. The transformation and softening temperatures both decreased linearly with increasing B_2O_3 content. YAS-6* had a T_g of $860^{\circ}C$ and a T_s of $910^{\circ}C$ while the values for YAB-E were $675^{\circ}C$ and $710^{\circ}C$, respectively.

2. Density

As shown in Fig. 8, the density of the YASB glasses decreased with increasing B_2O_3 content. Density is primarily a function of the density of the individual constituent oxides in a glass. The fact that YASB density decreases with increasing B_2O_3 content is logical, as the density of SiO_2 is 2.2 g/cm^3 and the density of B_2O_3 is 1.8 g/cm^3.

3. Vickers Microhardness

The Vickers Hardness Number of the YASB glasses decreased from 7.01 GPa to 6.08 GPa with increasing B_2O_3 content, as shown in Table III. The VHN varied with composition in the same way as the transformation and softening temperatures and the density.

4. Refractive Index

The refractive index of the YASB glasses changed from 1.663 to 1.675 with composition. The immersion liquids used to measure RI differed in 0.004 steps; so the RI difference (0.012) of the compositions, spanned three liquids. Fig. 9 is a graph of refractive index vs. composition. The highest and lowest values were for YAS-6* and YAB-E respectively.

5. Chemical Durability

The weight loss , at $30^{\circ}C$, of the YASB glasses in pH=1 HCl did not vary greatly with composition. Fig. 10 shows that the YASB-X glass and the YAS-6* glass had the highest and lowest weight loss, respectively. YASB-X collectively represents YASB-1 through YASB-10. YAS-6* had the lowest overall dissolution rate of 1.27×10^{-6} g/cm^{2}min, while the YASB glasses had a slightly higher overall value of approximately 1.68×10^{-6} g/cm^{2}min. These glasses exhibited the same weight loss behavior as the YAST glasses. Initially there was a greater weight loss, but after 2 or 3 days the rate became nearly constant. Individual chemical durability date is given in Appendix B.

6. Infrared (IR) Absorption Spectra

The IR spectra in Fig. 11 for YAB-E is nearly identical to that previously reported for YAB glasses.[7] The band spanning 1400-1200 cm^{-1} and the wide band from 1100-850 cm^{-1} have been attributed to B-O stretching in BO_3 and BO_4 groups, respectively. Bending of BO_3 groups is responsible for the absorption dip at 700 cm^{-1}.[7]

As the B_2O_3 content of the YASB glasses decreased, the influence of B-O stretching became less evident in the IR spectra (see Fig. 11). A dip appeared, at 950 cm^{-1}, for the YASB-7 glass which probably indicates a Si-O-B stretching mode.[13] This dip shifted down and became deeper for YASB-4, indicating the Si influence had become dominant. This trend continued for YAS-6* and was coupled with the disappearance of B-O effects. A second absorption dip appeared at 480 cm^{-1}, verifying the presence of

The four ^{27}Al spectra shown in Fig. 13 are very similar; each has three distinct peaks occurring at ≈ 55, 25 and 0 ppm. The reference for ^{27}Al was an $AlCl_3$ solid. The spinning speed was changed for one sample and the three major peaks remained, indicating they had no major contribution from spinning side bands. The smaller peaks, on either side of the three major ones, are spinning side bands. The peaks occurring at 55 and 0 ppm correspond with those reported previously,[14] and may indicate respective tetrahedral and octahedral coordination of the Al atoms. The reason for the existence of the central peak, at 25 ppm is unknown.

It would be interesting to further study the YASB glasses with NMR spectroscopy. The investigation of ^{89}Y and ^{11}B would be the next logical step. Unfortunately, instrument limitations prevented the pursuit of this project.

8. Glass Structure

From classical structural theories of glass formation, it can be assumed that SiO_2 and B_2O_3 act as network formers and Y_2O_3 and Al_2O_3 as network intermediates. Based on the measured IR data, Si is in 4-fold coordination and B is present in both 3 and 4-fold coordination. The radius-ratio rule suggests that Y, with a ratio of 0.68, is in 6-fold coordination.

Further structural data on the YASB glasses was obtained through NMR spectroscopy. Al was determined to be in both 4-fold and 6-fold coordination. It was also suggested that SiO_2 and B_2O_3 played similar roles in the structure of the lattice, further

verified by the fact that both are glass formers. NMR also

suggested that Y_2O_3 and Al_2O_3, as network intermediates, appear to

share similar positioning within the glass network.

IV. CONCLUSIONS

The density, refractive index and Vickers Hardness Number of the YASM glasses did not change drastically from the high values for the YAS eutectic composition.

TiO_2 additions to YAS produced a brown glass, whose density, refractive index, hardness and chemical durability increased with increasing TiO_2 content. YAST glasses could be devitrified to form a light gray, completely opaque, glass ceramic. The density, hardness and chemical durability were increased further by devitrification.

A series of YASB glasses were formed, holding Y_2O_3 and Al_2O_3 content constant. With increasing B_2O_3 content, the thermal expansion coefficient increased, whereas, the density, hardness, refractive index, transformation temperature, softening temperature and chemical durability decreased.

The YASM glasses are radio-opaque which makes them a candidate for fillers in dental restorative composites. Yttrium supplies the radio-opacity and M_xO_y allows manipulation of the refractive index to a suitable value.

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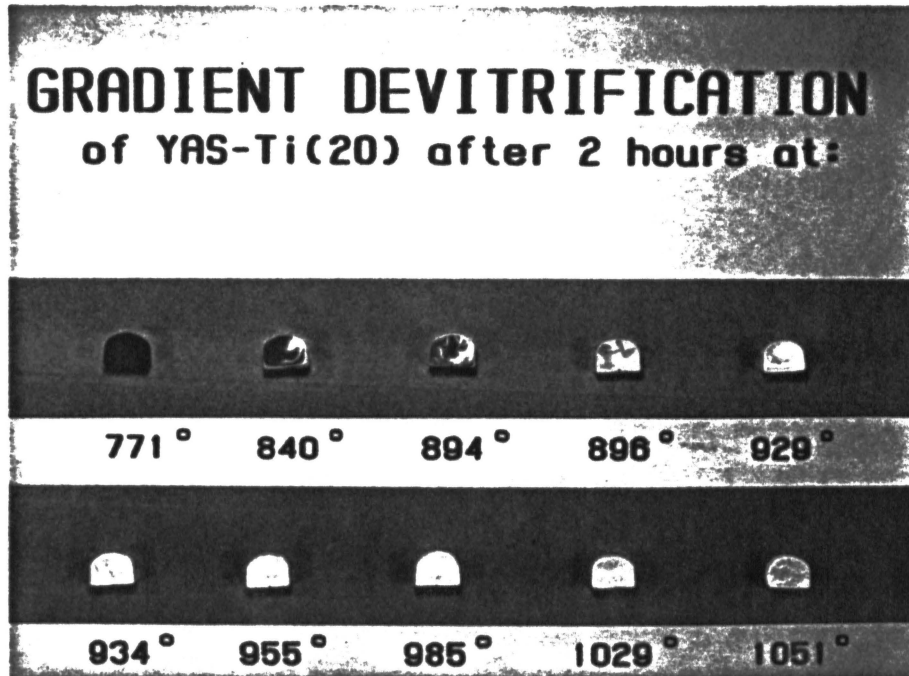
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various temperatures.
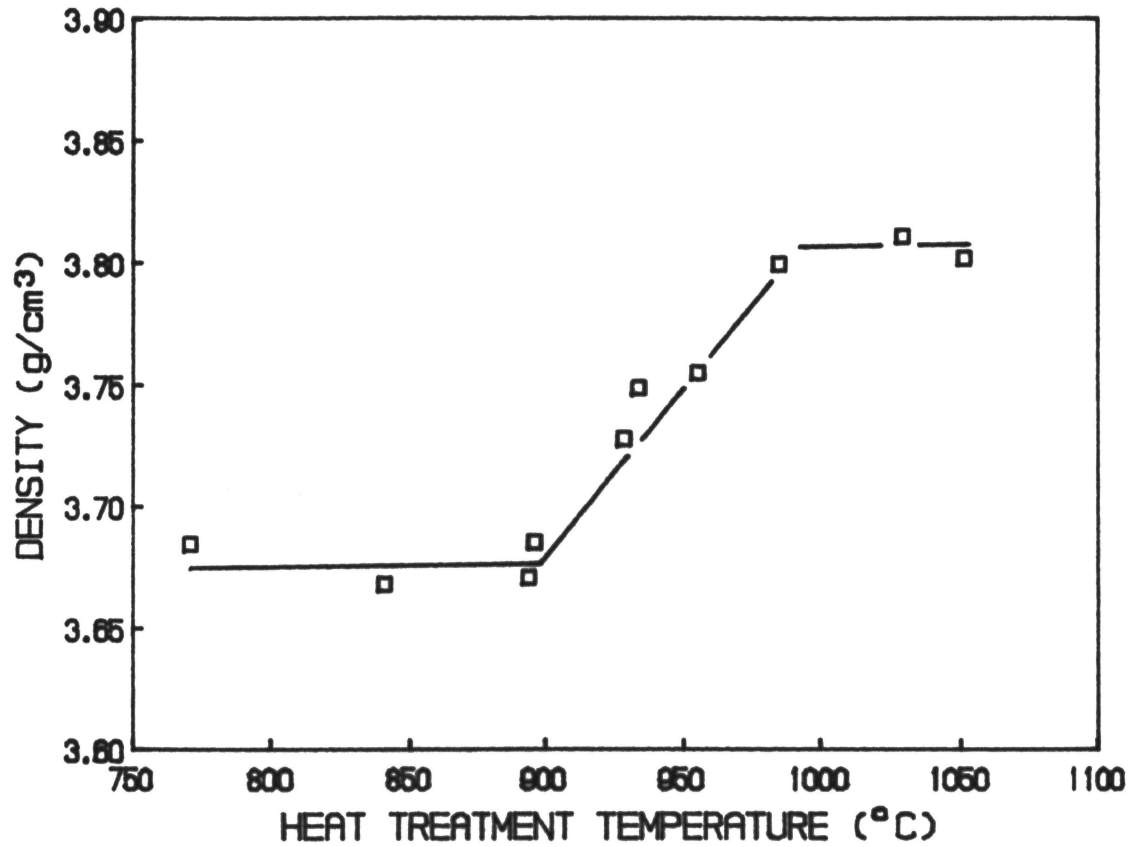
Fig. 2. Density of YAS-Ti(20) is shown as a function of heat treatment temperature, indicating the change that occurs by devitrification. Density values ±0.05.
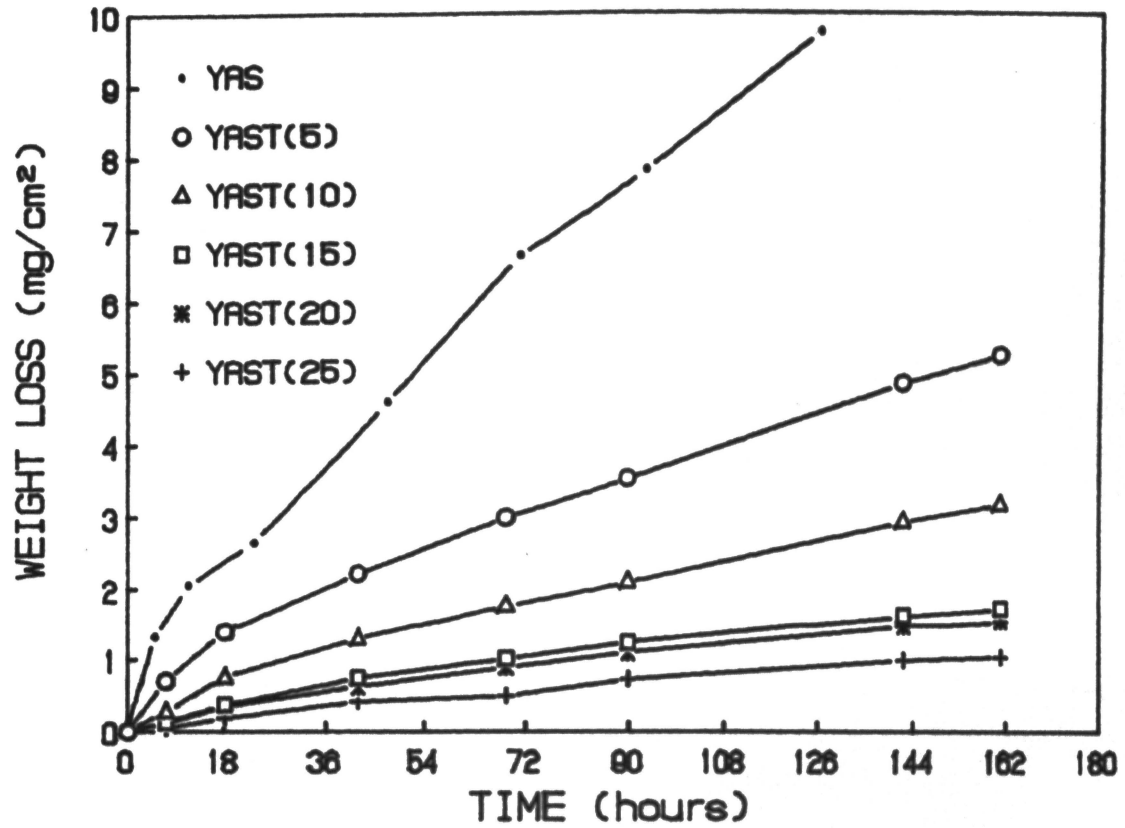
Fig. 3. Weight loss is shown as a function of time for YAST(x) glasses immersed in pH=1 HCl at 30°C.
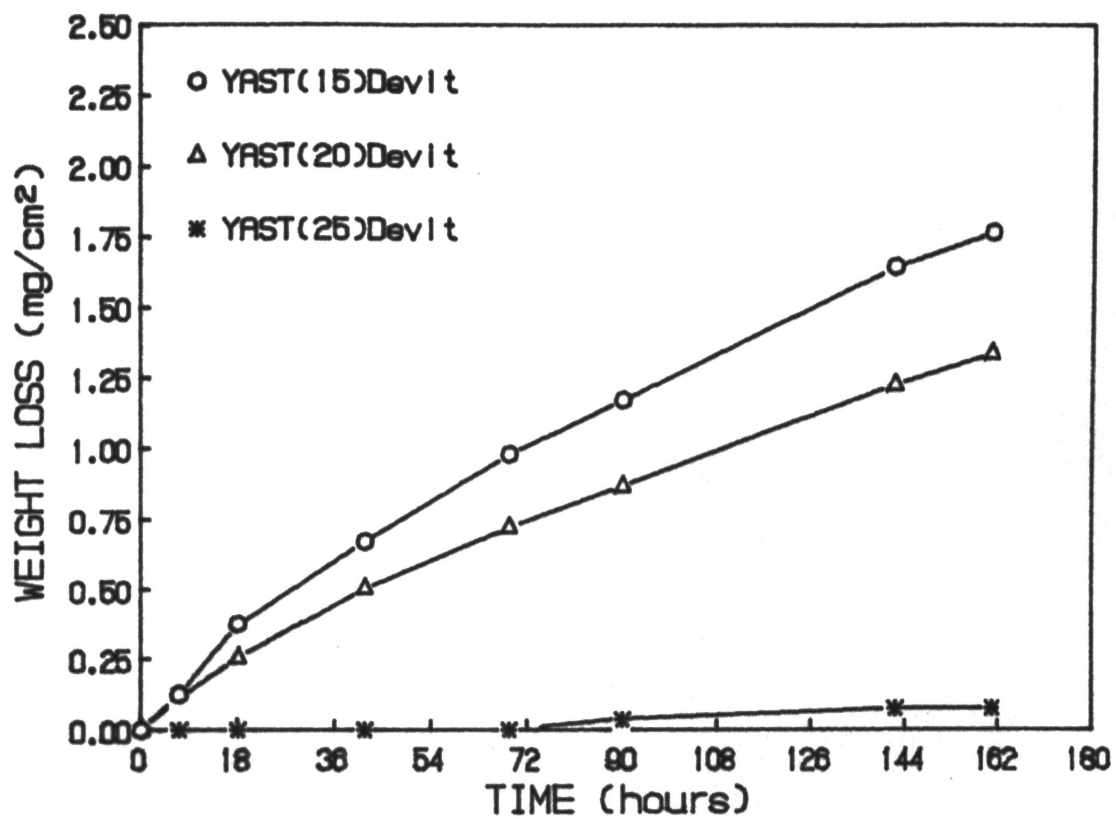
Fig. 4. Weight loss is shown as a function of time for YAST glass ceramics immersed in pH=1 HCl at 30°C.
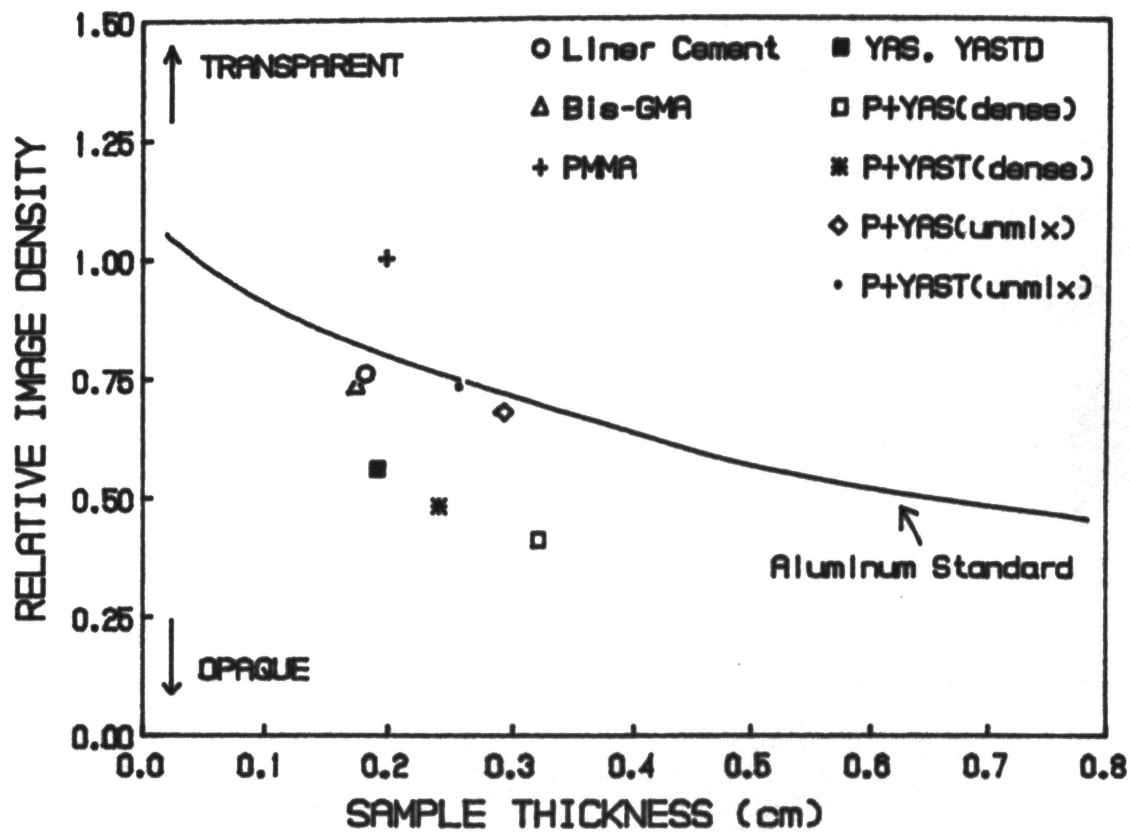
Fig. 5. Relative image density is shown as a function of sample thickness. Radiograph parameters are: 60 kV and 2.4 mA·min.
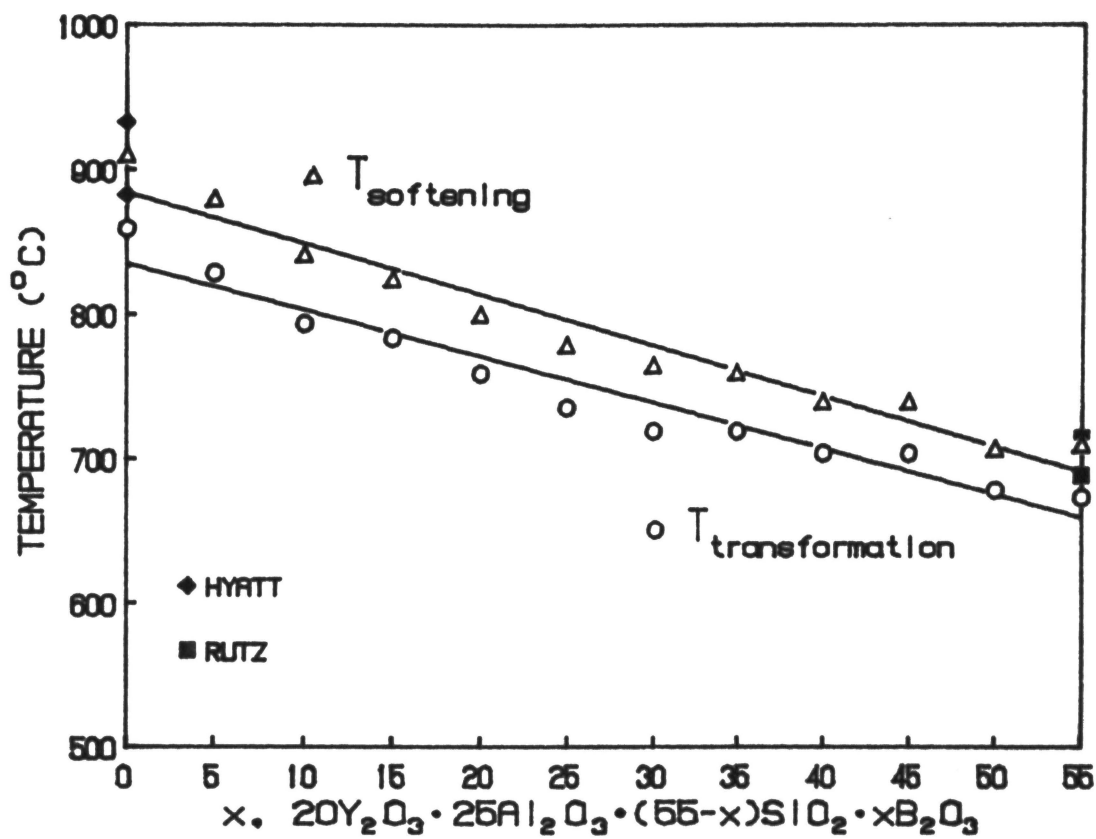
Fig. 6. Transformation and softening temperatures are shown as a function of composition for the YASB glasses.
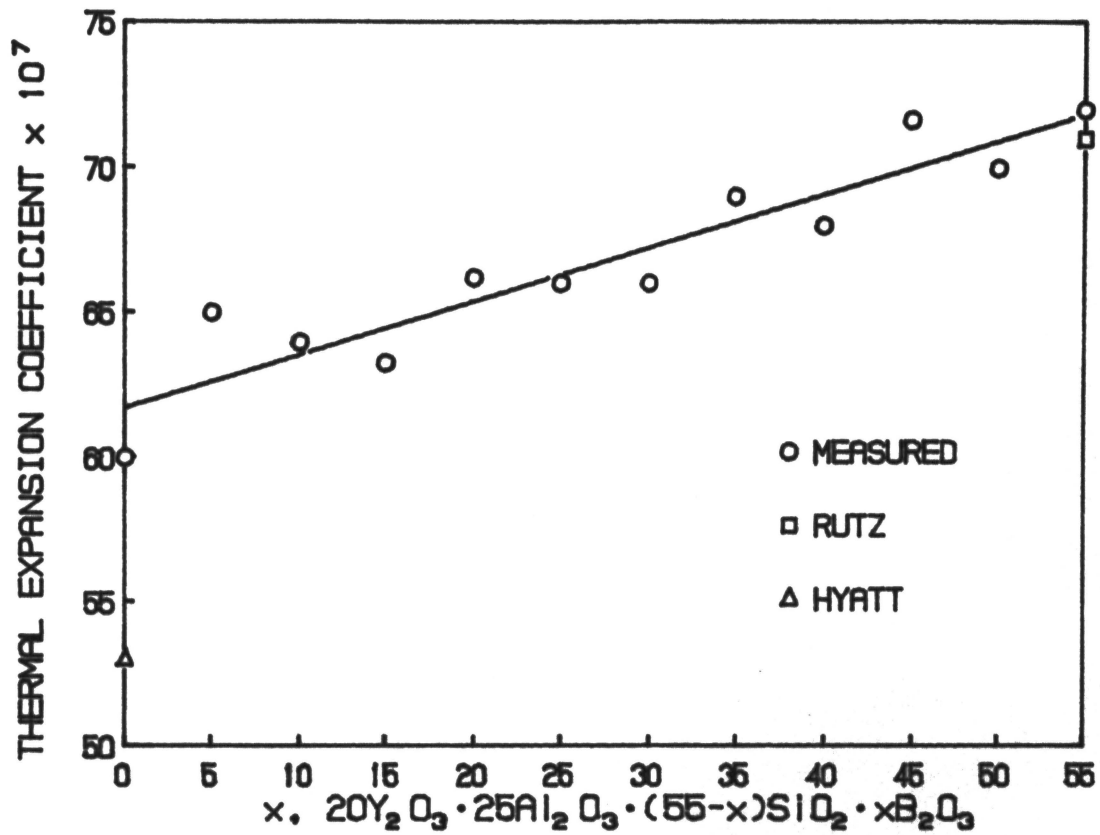
Fig. 7. Thermal expansion coefficient is shown as a function
of composition for YASB glasses.
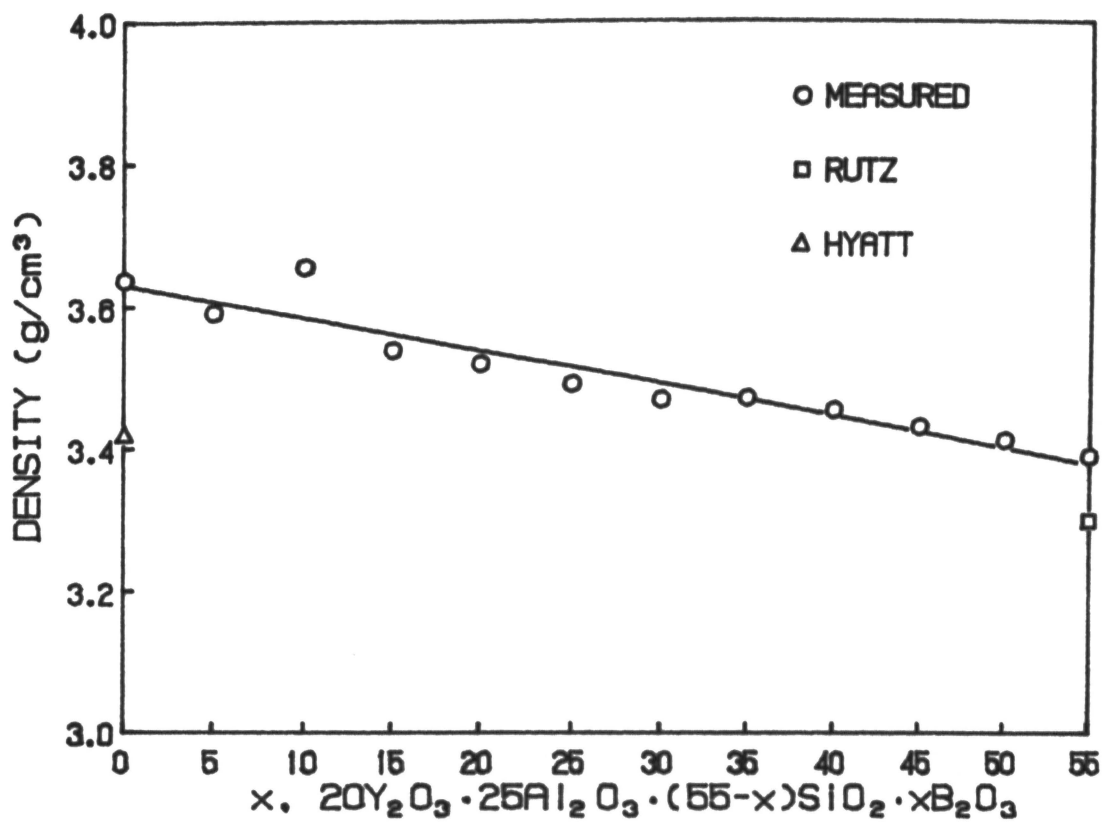
Fig. 8. Density is shown as a function of composition for the YASB glasses.
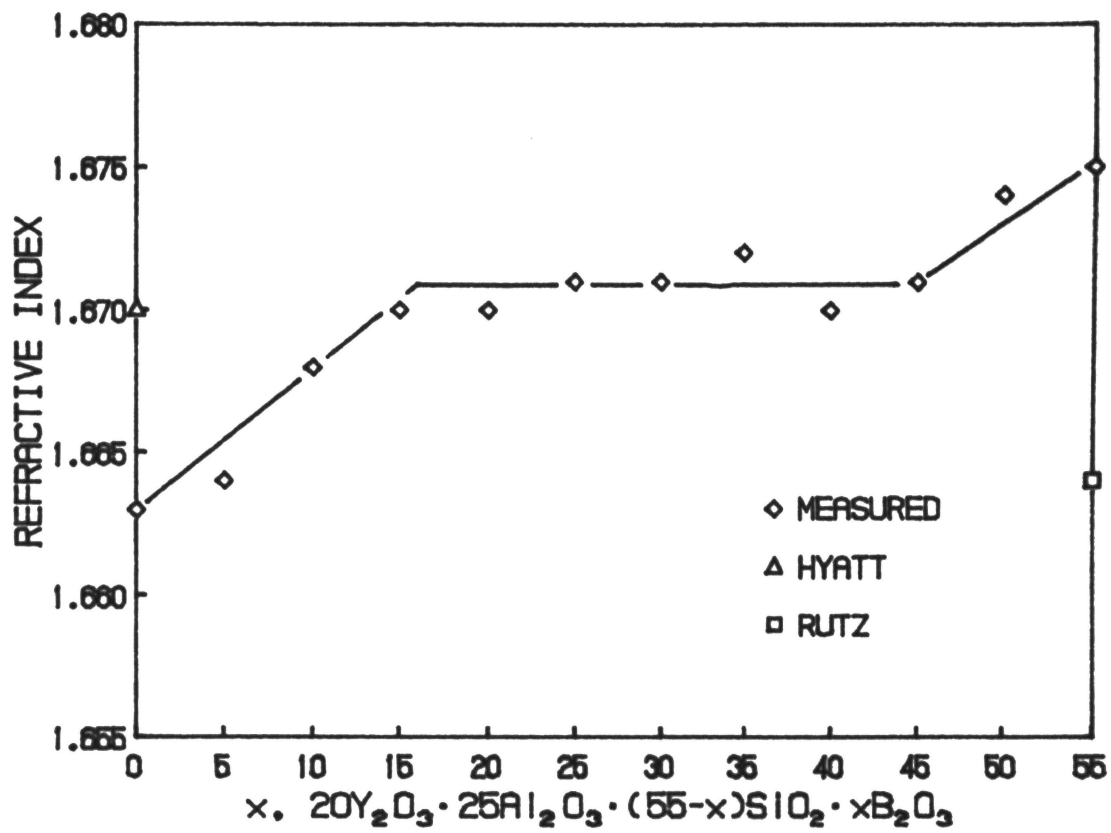
Fig. 9. Refractive index is shown as a function of composition for the YASB glasses.
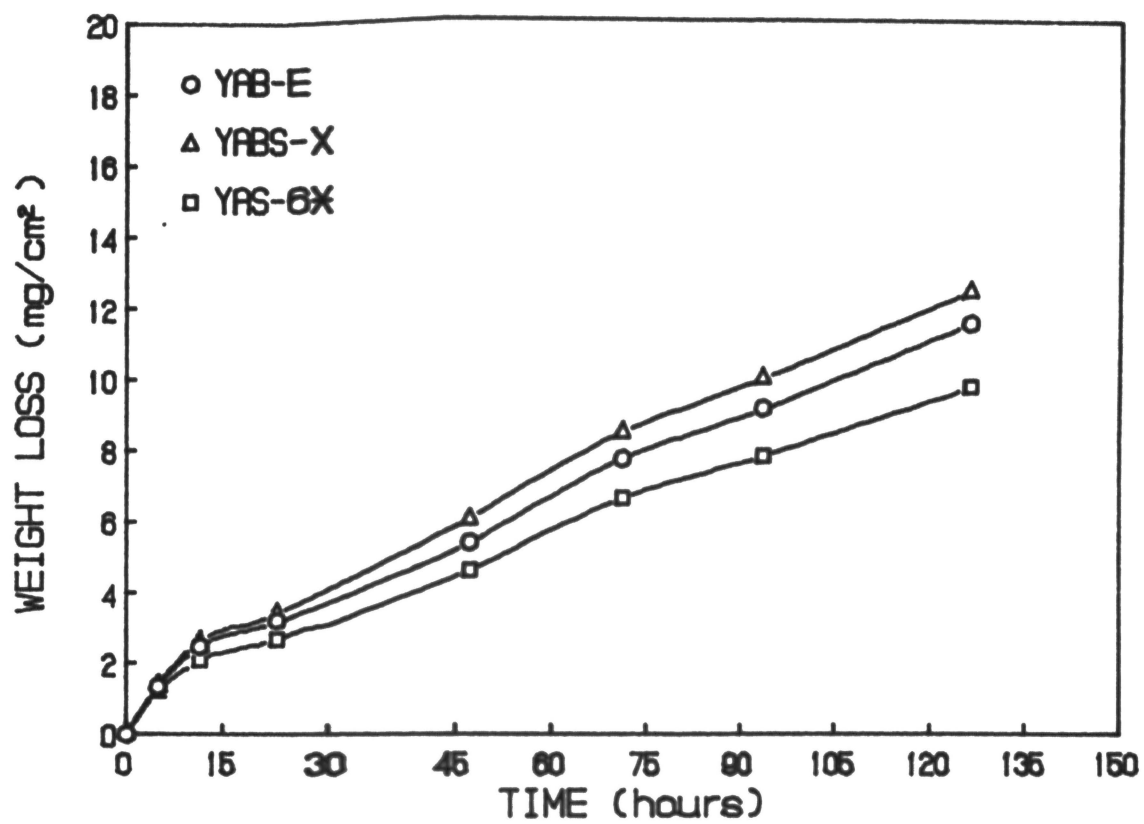
Fig. 10. Weight loss is shown as a function of time for
YAB-E, YASB—X and YAS-6* glasses immersed in pH=1 HCl at 30°C.
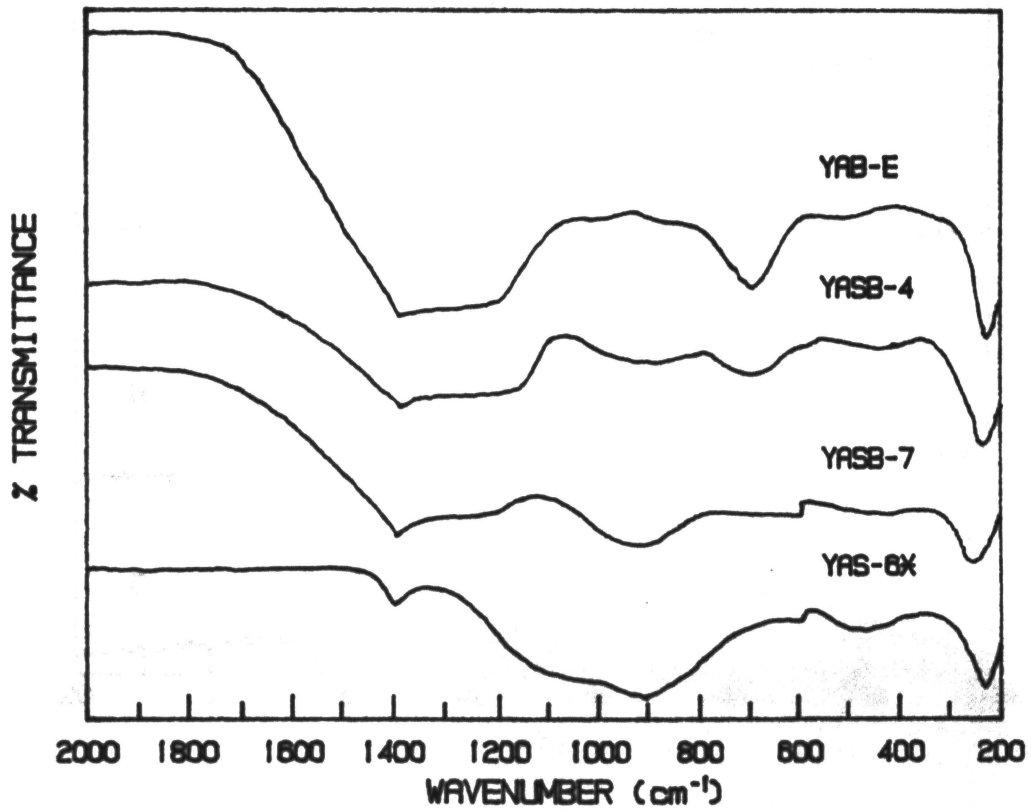
Fig. 11. Infrared absorption spectra of YASB glasses.
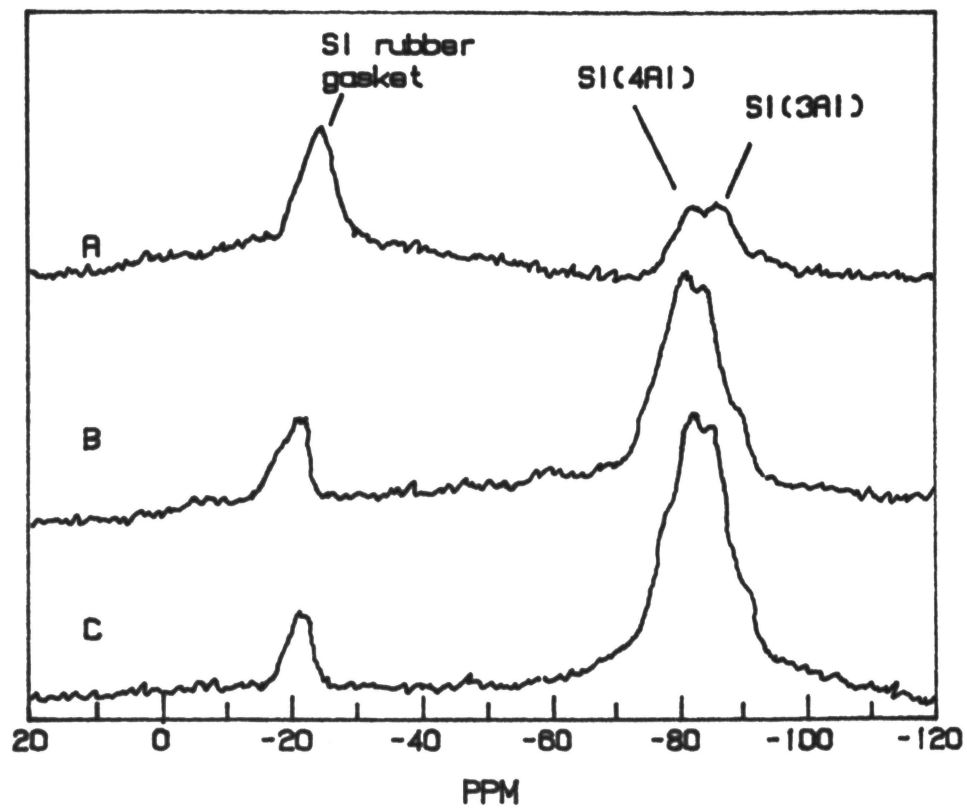
Fig. 12. ^{29}Si nuclear magnetic resonance spectra of;
(a) YASB-3, (b) YASB-7, (c) YAS-6*.
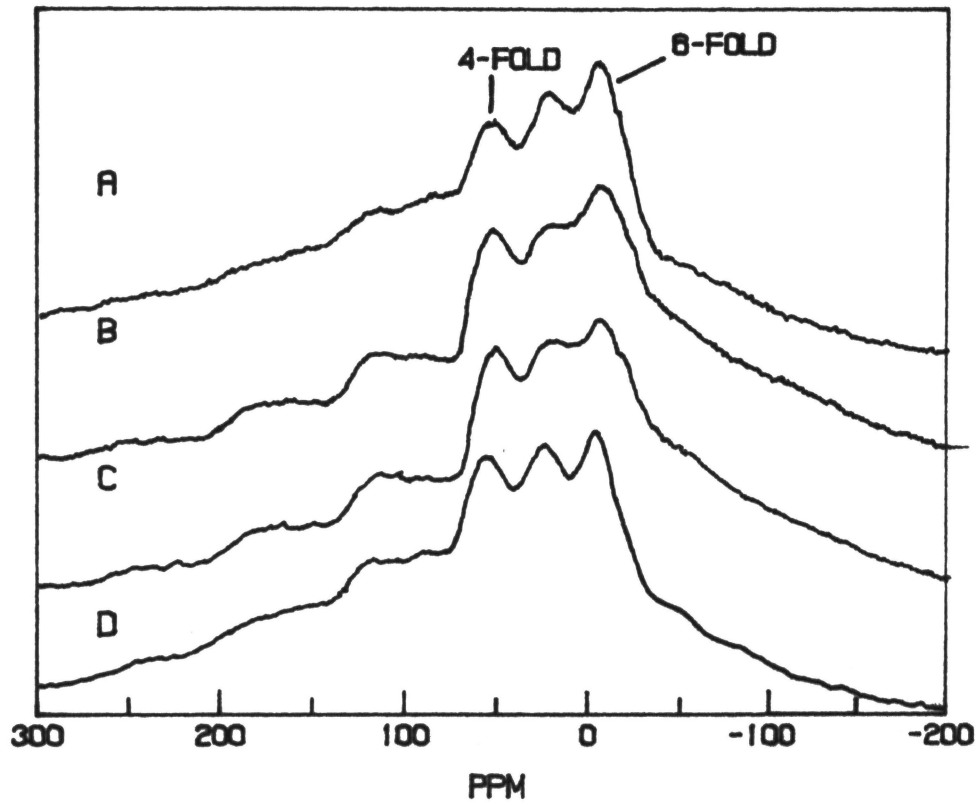
Fig. 13. ^{27}Al nuclear magnetic resonance spectra of;
(a) YAB-E, (b) YASB-3, (c) YASB-7, (d) YAS-6*.

TABLE I

COMPOSITIONS INVESTIGATED, GLASS FORMATION
CHARACTERISTICS, REFRACTIVE INDEX, VICKERS HARDNESS
NUMBER, AND DENSITY

COMPOSITION	FORMED GLASS	REMARKS	REFRACTIVE INDEX ±0.004	VHN GPa ±0.2	DENSITY g/cm^3 ±0.05
YAS	yes	homogeneous	1.65	6.85	3.52
YAS-Zn(10)*	yes	homogeneous	1.675	6.64	3.66
YAS-Ba(10)	yes	homogeneous	1.667	6.17	3.66
YAS-Ti(10)	yes	homogeneous	1.648	6.27	3.58
YAS-Ti(15)	yes	homogeneous	1.760	6.21	3.66
YAS-Ti(20)	yes	homogeneous	1.775	6.84	3.75
YAS-Pb(10)	yes	homogeneous	1.707	6.36	3.77
YAS-Sn(10)	yes	homogeneous	1.678	6.31	3.67
YAS-B(10)	yes	homogeneous	1.643	6.20	3.50
YAS-Sn(15)	no	crystallized prior to casting			
YAS-P(10)	no	crystallized prior to casting			
YAS-Zr(10)	no	contained unmelted raw material			
YAS-Ba(15)	no	crystallized prior to casting			
YAS-Zn(15)	yes	contained milky striations			
YAS-Ti(25)	no	partially crystallized upon casting			

* Nomenclature: YAS denotes eutectic base composition
  - M denotes M_xO_y addition
  (x) denotes the amount of M_xO_y in weight %

TABLE II

STRUCTURAL STATE, REFRACTIVE INDEX, VICKERS HARDNESS
NUMBER AND DENSITY OF YAST COMPOSITIONS

COMPOSITION	REMARKS	RI ±0.004	VHN GPa ±0.2	DENSITY g/cm^3 ±0.05
YAS	glassy	1.650	6.85	3.52
YAST(10)	glassy	1.648	6.27	3.58
YAST(15)	glassy	1.760	6.21	3.66
YAST(15)D	devitrified	nm	5.97	3.71
YAST(20)	glassy	1.775	6.84	3.75
YAST(20)D	devitrified	nm	7.10	3.80
YAST(25)D	devitrified	nm	8.28	3.86

nm = not measured

TABLE III

COMPOSITION, REFRACTIVE INDEX, VICKERS HARDNESS NUMBER
AND DENSITY OF YASB GLASSES

LABEL	COMPOSITION in mole %				RI ± 0.004	VHN GPa ± 0.2	DENSITY g/cm^3 ± 0.05
	Y_2O_3	Al_2O_3	SiO_2	B_2O_3			
YAB-E	20	25	0	55	1.663	nm	3.39
YASB-1	20	25	5	50	1.664	6.08	3.41
YASB-2	20	25	10	45	1.668	6.36	3.43
YASB-3	20	25	15	40	1.670	6.31	3.45
YASB-4	20	25	20	35	1.670	6.38	3.47
YASB-5	20	25	25	30	1.671	6.24	3.47
YASB-6	20	25	30	25	1.671	6.34	3.49
YASB-7	20	25	35	20	1.672	6.47	3.52
YASB-8	20	25	40	15	1.670	6.68	3.54
YASB-9	20	25	45	10	1.671	6.98	3.66
YASB-10	20	25	50	5	1.674	6.96	3.62
YAS-6*	20	25	55	0	1.675	7.01	3.64

nm = not measured

TABLE IV

TRANSFORMATION TEMPERATURE, SOFTENING TEMPERATURE AND
THERMAL EXPANSION COEFFICIENT OF YASB GLASSES

COMPOSITION	T_g, $\pm 5^{\circ}C$	T_s, $\pm 5^{\circ}C$	$\alpha \times 10^7$, $^{\circ}C^{-1}$
YAB-E	675	710	72
YASB-1	680	707	70
YASB-2	705	740	71.7
YASB-3	705	740	68
YASB-4	720	760	69
YASB-5	720	765	66
YASB-6	737	780	66
YASB-7	760	800	66
YASB-8	785	825	63.3
YASB-9	795	842	64
YASB-10	830	880	66.7
YAS-6*	860	910	60

VITA

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She has been enrolled in the Graduate Scool of the University of Missouri-Rolla since January 1986 and has been funded by the state of Missouri through the Graduate Center for Materials Research and the Ceramic Engineering Department.

APPENDIX A

TOTAL WEIGHT CHANGE, TOTAL WEIGHT LOSS, AND OVERALL AVERAGE DISSOLUTION RATE OF YAST COMPOSITONS IMMERSED IN pH=1 HCl AT 30°C

YAS; $A=2.886 \text{ cm}^2$

time hours	total weight change mg	total weight loss $g/cm^2 \times 10^3$	overall average dissolution rate $g/cm^2 min \times 10^7$
5	3.4	1.18	39.3
11.25	5.9	2.04	30.3
23.25	7.6	2.63	18.8
47	13.2	4.57	16.2
71	19.0	6.58	15.4
93.5	22.4	7.76	13.8
126.5	27.9	9.67	12.7

YAST(5); $A=2.299 \text{ cm}^2$

7	1.6	0.70	16.6
18	3.2	1.39	12.9
41.5	5.1	2.22	8.90
68.5	6.9	3.00	7.30
89.75	8.1	3.52	6.56
142.25	11.2	4.87	5.70
160.75	12.1	5.26	5.45

YAST(10); $A=3.334 \text{ cm}^2$

7	0.9	0.27	6.43
18	2.5	0.75	6.95
41.5	4.3	1.29	5.18
68.5	5.9	1.77	4.30
89.75	7.0	2.10	3.90
142.25	9.8	2.94	3.45
160.75	10.6	3.18	3.30

YAST(15); A=5.590 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x10^3	overall average dissolution rate g/cm^{2}min x 10^7
7	0.7	0.12	2.98
18	2.1	0.38	3.47
41.5	4.1	0.73	2.95
68.5	5.6	1.00	2.43
89.75	6.9	1.23	2.28
142.25	9.3	1.66	1.95
160.75	9.1	1.63	1.68

YAST(15)D; A= 4.019 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x10^3	overall average dissolution rate g/cm^{2}min x 10^7
7	0.5	0.12	2.97
18	1.5	0.37	3.45
41.5	2.7	0.67	2.70
68.5	3.9	0.97	2.37
89.75	4.7	1.17	2.17
142.25	6.6	1.64	1.92
160.75	7.1	1.77	1.83

YAST(20); A=4.312 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x10^3	overall average dissolution rate g/cm^{2}min x 10^7
7	0.4	0.11	2.22
18	1.5	0.35	3.22
41.5	2.7	0.63	2.52
68.5	3.8	0.88	2.15
89.75	4.7	1.09	2.02
142.25	6.3	1.46	1.72
160.75	6.6	1.53	1.58

YAST(20)D; A=2.765 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x 10^3	overall average dissolution loss g/cm^{2}min x 10^7
7	0.3	0.11	2.58
18	0.7	0.25	2.35
41.5	1.4	0.51	2.03
68.5	2.0	0.72	1.77
89.75	2.4	0.87	1.62
142.25	3.4	1.23	1.43
160.75	3.7	1.34	1.38

YAST(25); A=2.218

7	0.1	0.05	1.07
18	0.4	0.18	1.67
41.5	0.9	0.41	1.63
68.5	1.1	0.50	1.20
89.75	1.6	0.72	1.33
142.25	2.2	0.99	1.17
160.75	2.3	1.04	1.08

YAST(25)D; A=2.684 cm^2

7	0	0	0
18	0	0	0
41.5	0	0	0
68.5	0	0	0
89.75	0.1	0.04	0.07
142.25	0.2	0.07	0.09
160.75	0.2	0.07	0.08

APPENDIX B

TOTAL WEIGHT CHANGE, TOTAL WEIGHT LOSS AND OVERALL
AVERAGE DISSOLUTION RATE OF YASB GLASSES IMMERSED IN
pH=1 HCl AT 30°C

YAB-E; A=2.827 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x 10^3	overall average dissolution rate g/cm^2 min x 10^7
5	3.8	1.34	44.8
11.25	6.9	2.44	36.2
23.25	9.0	3.18	22.8
47	15.2	5.38	19.0
71	21.8	7.71	18.2
93.5	25.8	9.12	16.3
126.5	32.6	11.53	15.2

YASB-2; A=2.935

5	3.8	1.30	43.2
11.25	7.0	2.38	35.3
23.25	9.8	3.34	30.2
47	17.5	5.96	21.2
71	25.4	8.65	20.3
93.5	30.3	10.32	18.3
126.5	37.3	12.71	16.7

YASB-3; A=2.645 cm^2

5	3.5	1.32	44.3
11.25	6.2	2.34	34.7
23.25	7.7	2.91	20.8
47	15.6	5.90	20.8
71	22.5	8.51	20.0
93.5	26.5	10.0	17.8
126.5	33.8	12.8	16.8

YASB-5; A=2.305 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x 10^3	overall average dissolution rate g/cm^{2}min x 10^7
5	2.9	1.26	42.0
11.25	5.5	2.39	35.3
23.2	7.4	3.21	23.0
47	13.0	5.64	20.0
71	19.2	8.33	19.5
93.5	22.6	9.80	17.5
126.5	28.0	12.2	16.0

YASB-6; A=2.958 cm^2

5	3.8	1.28	42.8
11.25	6.9	2.33	34.5
23.25	9.5	3.21	23.0
47	16.9	5.71	20.3
71	24.4	8.25	19.3
93.5	29.0	9.80	17.5
126.5	37.0	12.51	16.5

YASB-7; A=2.967 cm^2

5	4.1	1.38	46.0
11.25	7.7	2.60	35.0
23.25	10.2	3.44	24.7
47	18.0	6.07	21.5
71	25.1	8.46	19.8
93.5	29.6	9.98	17.8
126.5	36.9	12.44	16.3

YASB-8; A=2.850 cm^2

time hours	total weight change mg	total weight loss g/cm^2 x 10^3	overall average dissolution rate $g/cm^2 min$ x 10^7
5	4.9	1.72	57.3
11.25	8.3	2.91	43.2
23.25	10.9	3.82	27.3
47	15.9	5.58	19.8
71	25.6	8.98	21.0
93.5	31.3	10.98	19.5
126.5	39.7	13.93	18.3

YASB-9; A=2.743 cm^2

5	3.4	1.24	41.3
11.25	6.2	2.26	33.5
23.25	8.4	3.06	22.0
47	15.3	5.58	19.8
71	22.3	8.13	19.2
93.5	26.5	9.66	17.2
126.5	33.7	12.29	16.2

YAS-6[*]; A=2.886 cm^2

5	3.4	1.18	39.3
11.25	5.9	2.04	30.3
23.25	7.6	2.63	18.8
47	13.2	4.57	16.2
71	19.0	6.58	15.4
93.5	22.4	7.76	13.8
126.5	27.9	9.67	12.7