

Transparent Yttria for IR Windows and Domes – Past and Present

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ABSTRACT

Yttria (Y_2O_3) has excellent optical performance through the full mid wavelength infrared (MWIR) atmospheric transmission band at both ambient and elevated temperatures. Current state-of-the-art yttria's thermomechanical properties are adequate for a number IR window and dome applications, but only marginal for the most demanding missions. The first full-scale missile domes of transparent yttria manufactured from ceramic powders were developed in the 1980's under Navy funding. Raytheon perfected and characterized its undoped polycrystalline yttria, while lanthana-doped yttria was similarly developed by GTE Laboratories. The two versions have comparable infrared transmittance, mechanical properties, and thermal expansion, while the undoped material exhibited 2 times higher thermal conductivity. Although conventional yttria's strength and hardness are lower than the more durable but less transmitting MWIR materials (sapphire, ALON, spinel), its thermal shock performance is similar. In fact, 7 out of 7 flat yttria windows were successfully wind-tunnel tested under hypersonic conditions simulating representative surface-to-air interceptor missile flights. Recent renewed interest in yttria windows and domes has prompted efforts to enhance mechanical properties by producing materials with micron or nano-size grains. Three vendors were selected to provide nanoscale powders for testing and evaluation, and they were compared to a conventional (5 μm) yttria powder previously used to prepare transparent ceramic yttria. While all of the nanopowders evaluated had impurity levels that were too high to allow processing to full transparency, two were processed to full density and moderate transparency. Samples were sintered to a closed pore state at temperatures as low as 1400°C. Ultrasonic attenuation as a technique for measuring particle size distributions in slurries was explored and found to be an invaluable tool when processing colloidal suspensions of nanopowders. In this paper, the optical, thermal, and mechanical properties of conventional transparent yttria are reviewed and compared with other candidate MWIR window/dome materials. The status of on-going Navy-sponsored development of nano-grain yttria is also presented.

(1) Initial Development of Transparent Yttrium Oxide

The initial work in developing transparent yttrium oxide ceramics was carried out by General Electric in the 1970's, motivated by lighting and ceramic laser applications. Greskovich and Woods [1] fabricated transparent yttrium oxide containing approximately 10% thorium oxide, which they called Yttralox.

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The additive served to control grain growth during densification, so that porosity remained on grain boundaries and not trapped inside grains where it would be very difficult to eliminate during the final stages of sintering. Typically, as ceramics densify during heat treatment, grains grow in size while the remaining porosity decreases in both volume fraction and size. Most engineering ceramics are considered to be fully dense when they reach 98-99 percent of theoretical density (%TD). However, the remaining porosity in these ceramics is typically on the order of 1 micron in size, which is extremely efficient at scattering light. Therefore, optically transparent ceramics must be truly 100% dense with no pores remaining.

GE's transparent Yttralox was followed by GTE's lanthana-doped yttria [2], also intended for lighting applications and also contained approximately 10 percent additive to control grain growth and facilitate elimination of porosity. Both the GE and GTE transparent yttria ceramics required extended firing times at temperatures above 2000°C.

Interest in transparent yttrium oxide ceramics for IR guided missile during the 1980's was prompted by the need for domes that are fully transmitting through the entire 3-5 micron mid wavelength infrared (MWIR) atmospheric band. Full transmittance out to 5 microns wavelength and beyond is important to maximize the signal, but much more important to minimize the noise from hot dome emission at those wavelengths that are even modestly absorbed by the dome. As seen in Figure 1, the existing more durable MWIR materials (sapphire, ALON, spinel) are not fully transparent at 5 microns. In oxides, as well as other compounds, there is in fact a general trade-off between longer longer wavelength transmission and mechanical durability.

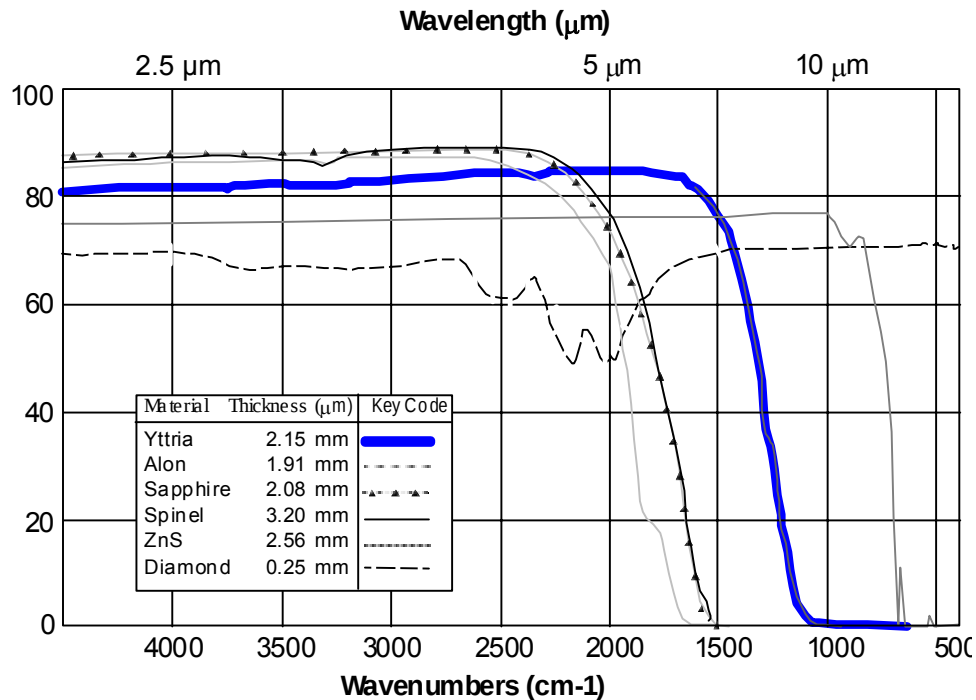


Figure 1: Transmission spectra for several IR window materials, with yttria shown in blue. Among the oxides, there is a general trade-off between the long wavelength cut-off and durability.

Yttria and lanthana-doped yttria were developed as infrared dome materials because of their superior infrared transmission range in comparison to those of sapphire, ALON, and spinel. Beginning in 1985, both Raytheon and GTE were funded to develop transparent yttrium oxide missile domes. Raytheon's approach was to avoid additives, because of the substantial negative effect on thermal conductivity generally observed in oxide solid solutions (Figure 2). Instead, Raytheon utilized the sinter + HIP approach to fabricate 100% dense, porosity-free ceramics. In this method, the green ceramic is first sintered to approximately 95%TD, in which the remaining porosity consists of isolated, closed pores. Closed pore density in undoped yttrium oxide can be achieved by firing at 1700°C for less than 1 hour. After the relatively short sintering run, the component is placed in a hot isostatic press (HIP) and processed for 3-10 hours at ~30 kpsi (~200 MPa) at a temperature similar to that of the initial sintering. The applied isostatic pressure provides additional driving force for densification by substantially increasing the atomic diffusion coefficients. Using the sinter + HIP method, transparent yttria ceramics are produced at lower temperatures, shorter total firing times, and without thermal-conductivity-reducing additives.

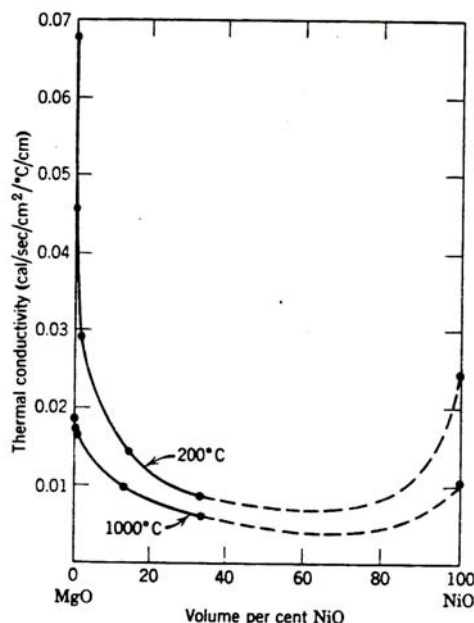


Figure 2: Thermal conductivity of the MgO-NiO mixed oxide system, showing the dramatic reduction in conductivity in ternary systems with even small substitutions for either binary end member.

During the Navy program, both Raytheon and GTE successfully fabricated transparent domes as well as a variety of specimens for optical, mechanical, and thermal testing. Figure 3 shows a 3-inch transparent undoped yttria dome produced by Raytheon using the sinter + HIP method.



Figure 3: Transparent undoped yttria dome fabricated by Raytheon in the mid 1980's.

A thorough comparative study of transparent yttria properties is contained in two Navy Technical Publications [3,4], which describe tests of fully dense, transparent, polycrystalline yttria (Y_2O_3 , produced by Raytheon) and lanthana-doped yttria ($0.9 \text{ Y}_2\text{O}_3$ -- $0.1 \text{ La}_2\text{O}_3$, produced by GTE). The two materials were found to have similar infrared optical properties, but the visible transmission of lanthana-doped yttria was superior to that of undoped yttria (Figure 4). Thermal and mechanical properties were also similar, except for thermal conductivity and strength. The thermal conductivity of undoped yttria is 2.5 times greater than that of lanthana-doped yttria at 300 K, and 30% greater at 1400 K (Figure 5). Lanthana-doped yttria is 40% stronger than undoped yttria at 300 K, although the Weibull modulus of the undoped yttria is larger. At elevated temperatures, undoped yttria appeared to be slightly stronger.

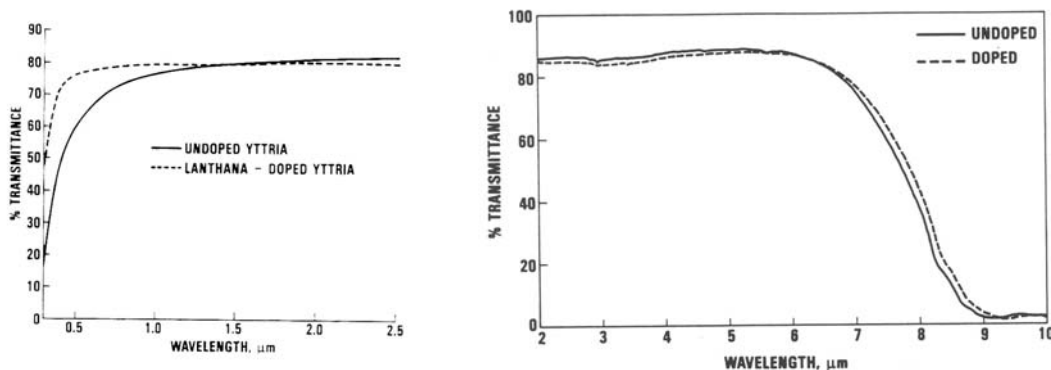


Figure 4: Visible and infrared transmittance of undoped and lanthana-doped yttria. The doped version had superior visible transmittance, but both materials were comparable in the infrared.

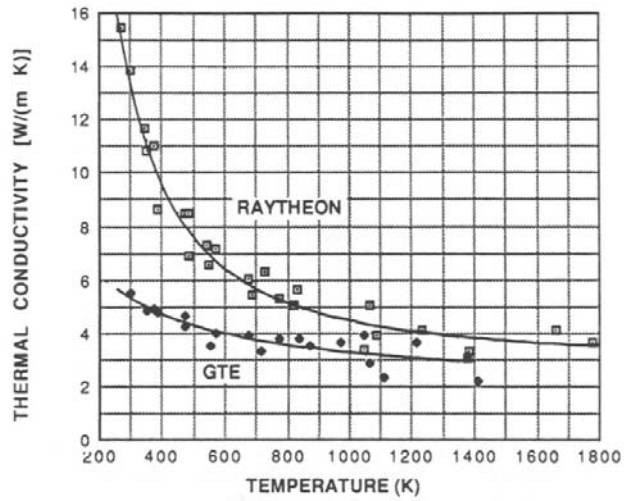


Figure 5: Thermal conductivity of Raytheon undoped and GTE lanthana-doped yttria as a function of temperature. The undoped version exhibits substantially greater conductivity, particularly at ambient temperatures.

Full scale domes of both materials survived wind tunnel tests corresponding to Mach 5 speed at an altitude of 50,000 feet (stagnation heat transfer = 80 Btu/ft²/s = 11.4 kJ/m²/s), but failed in more severe tests. Aerothermal analysis based on the measured properties of yttria was in satisfactory agreement with observed behavior in the wind tunnel.

Selected property data, for which the two yttria materials showed statistically significant differences, are summarized in Table 1.

Table 1. Property Differences for Undoped (Raytheon) and Lanthana-Doped (GTE) Yttria
From NWC TP 7002 [3]

Refractive Index at 3.39- μ m Wavelength

<u>Raytheon</u>	<u>GTE</u>
1.869	1.90 (estimated)

Representative Total Integrated Scatter, 2-mm thick specimen

<u>Wavelength, μm</u>	<u>Raytheon</u>	<u>GTE</u>
0.63	20%	10%
1.15	7%	7%
3.39	2%	2%

Thermal Conductivity W/(m-K)

Raytheon: (T = 270-1800 K):	Conductivity = $2.86 + 8.566 \times 10^{-4} T^{-1.577}$
GTE: (T = 270-1400 K):	Conductivity = $1.10 + 100.3 T^{-0.5577}$

Thermal Expansion (T = 300-2300 K) (initial length, L, measured at 294 K)

Raytheon:	$\Delta L/L = -1.492 \times 10^{-3} + 4.040 \times 10^{-6} T + 3.225 \times 10^{-9} T^2 - 5.508 \times 10^{-13} T^3$
GTE:	$\Delta L/L = -1.757 \times 10^{-3} + 5.276 \times 10^{-6} T + 1.974 \times 10^{-9} T^2 - 1.896 \times 10^{-13} T^3$

Density at 294 K

Raytheon:	5.024 ± 0.004 g/cc	(Theoretical = 5.033)
GTE:	5.14 ± 0.03 g/cc	(Theoretical = 5.126)

4-Point Bending Flexural Strength MPa ($\pm$ standard deviation for 5 measurements)

<u>Temperature, K</u>	<u>Raytheon</u>	<u>GTE</u>
294	74 ($\pm$ 30%)	98 ($\pm$ 10%)
811	101 ($\pm$ 26%)	95 ($\pm$ 14%)
1366	130 ($\pm$ 12%)	123 ($\pm$ 19%)
1922	59 ($\pm$ 25%)	55 ($\pm$ 12%)

Equibiaxial Flexural Strength (measured at 294 K with 19-mm diameter x 2.0-mm thick disks using load ring diameter = 7.72 mm and support ring diameter = 15.4 mm)

	<u>Raytheon</u>	<u>GTE</u>
Average strength, MPa	117	164
Number of disks	28	24
Standard deviation	14%	23%
Weibull modulus	7.6	4.3

2. Uncooled Yttria Flat Windows for Hypersonic Missiles

A small flat window geometry has the potential to eliminate the need for window cooling for hypersonic interceptors. If the complexity and increased weight of the cooling system can be eliminated, the missile system unit cost can be significantly lowered. Figure 6 shows an IR seeker innovation developed and fabricated by Raytheon that allows a small flat window to be used for a missile that requires angle of attack (AOA), i.e., simultaneously allowing reasonable optical aperture, large look angle range, and a small window diameter. Analyses indicate robust performance of the IR window and seeker that would significantly expand the IR seeker operational regime. Figure 8 shows the results of an engineering model assessment of the flat window survival limits. The window is most susceptible to tensile stress failure generated by thermally shocking the window when it is initially exposed to the air stream. The model predicts yttria window survival: (1) at Mach 4, sea level; (2) at Mach 5 for altitudes above 23 Kft; (3) at Mach 6 for altitudes above approximately 36 Kft. Figure 7 shows the hardware used in proof-of-concept tests completed in the JHU/APL Cell 4 supersonic wind tunnel. The facility allows testing the full-scale flat window. In these tests, full scale flight prototype windows were evaluated using a subscale fore body limited to zero AOA. Calorimeters were used to define the heating distribution on the window, and yttria window survival was demonstrated in the tests. The anticipated aero thermal response of the flat window geometry on a full-scale fore body at non-zero AOA was assessed with computational fluid dynamics (CFD). Figure 9 shows a CFD simulation of the flow surrounding the flat window mounted on missile fore body at 7° AOA, i.e., the window pitched toward the oncoming flow.

Seven flat, circular undoped yttria windows (2.37-inch diameter by 0.16-inch thick) fabricated by Raytheon were subjected to successive hypersonic wind tunnel tests simulating the full range of missile interceptor trajectories. In all 7 tests, the yttria window survived the wind-tunnel-induced thermal shock.

One window developed a crack as it was cooled from the test conditions, but remained intact through the cool down as well as the test. This single instance of cracking, would not have impacted performance had the test been an actual flight. It does, however, demonstrate that the test conditions may have been subjecting the conventionally processed material to thermal stress levels approaching a durability limit. Though additional testing would be required to fully quantify limits for the material, the results make a strong case for development of yttria windows that exhibit improved thermal shock resistance. These would provide both additional margin for existing flight conditions and room for expansion into more aggressive trajectories in future missile systems.

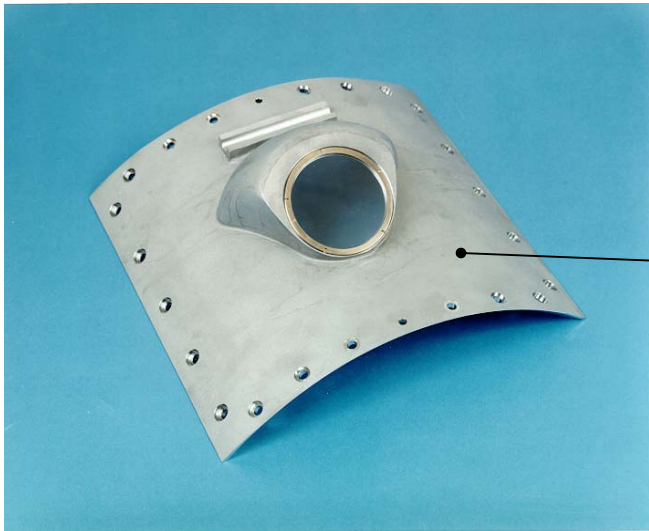


Figure 6. Raytheon flight prototype test hardware showing a circular yttria flat window mounted at 30 degrees.

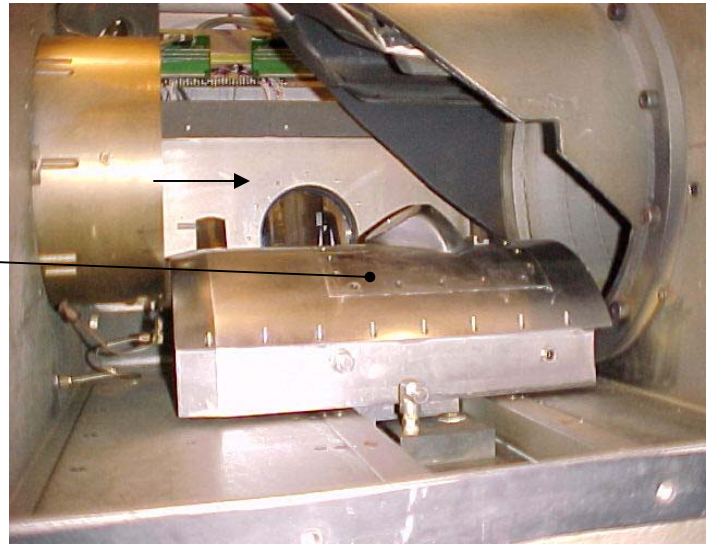


Figure 7. Test hardware setup in JHU/APL Cell 4 wind tunnel.

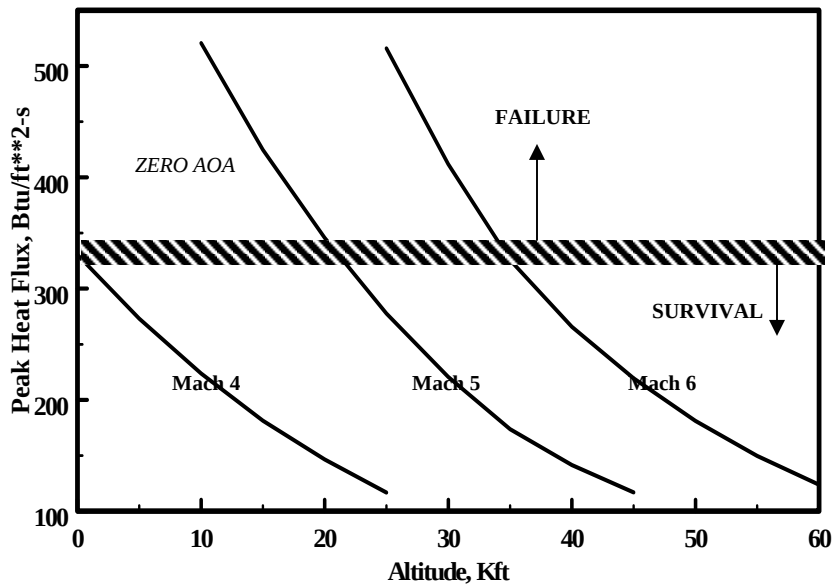


Figure 8. Thermal shock boundaries for a 30° mounted, 0.16-inch thick yttria window.

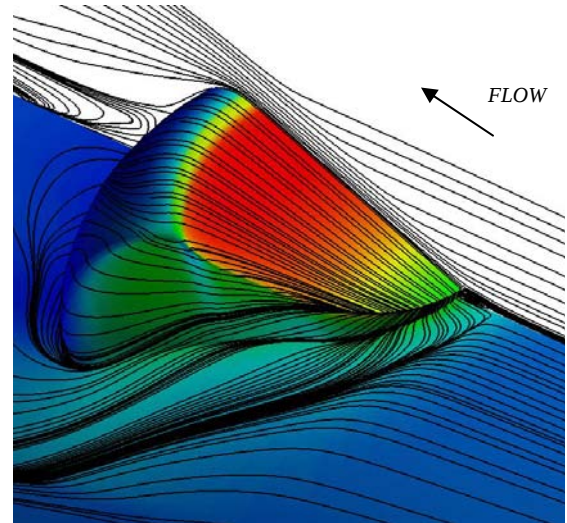


Figure 9. CFD flow and surface pressure contours at 7° AOA fore body orientation.

3. Nano-grained Transparent Yttria Development

It is well known that fracture strength of ceramics increases as their grain size is reduced. Strength improvements in the range 2-3X are common and increases of up to 5X have been demonstrated in some materials. Thermal shock resistance increases in proportion to strength. For typical ceramic systems, grain sizes in the 1-10 μm range produce near maximum strengths. By processing yttria beginning with nano-sized (<100 nm) powders and carefully controlling grain growth during high temperature processing, it should be possible to retain the desirable MWIR optical properties, while enhancing the mechanical properties for use in the most aggressive missile trajectories. To that end, under a recent Navy funded program, an effort was made to prepare optical quality ceramic yttria with a grain size small enough to maximize the strength and expand its potential applications as a MWIR material [5]. This work focused on the characterization of available yttria nanopowders as well as densification behavior.

Three yttria nanopowder vendors, referred to as Nano-1, Nano-2, and Nano-3, were chosen to provide initial samples. All the powders were white in color. Nano-1 was produced using a patented flame spray pyrolysis process and had a bulk density of 0.15 g/cc. Nano-2 was produced by a chemical vapor condensation (CVC) process, using precursors reacted in a flat flame burner, and had an even lower bulk density of 0.13 g/cc. Nano-3, produced by the precipitation of a precursor and calcination at high temperature, was markedly different in appearance, with a higher bulk density and exhibiting hard agglomerates of partially sintered crystallites.

Previous experience [6-8] in producing conventional transparent yttria indicated that purity of the starting powder was critical to producing material with good transmission properties and minimal scatter. Even minute quantities of second phase can cause substantial scatter. Impurity testing was performed on samples of yttria nanopowders from three different vendors and compared to that of two conventional micron-size powders (Conv-1 and Conv-2). The samples were tested via glow discharge mass spectrometry (GDMS). Each nanopowder had a different variety of impurities at levels beyond that considered acceptable, with at least one impurity an order of magnitude greater than the goal in each sample. The major impurities found in the various powders are summarized in Table 2. For silicon, the excess over the goal value is shown as a multiple. Past experience indicates that aluminum and/or silicon levels greater than approximately 100 ppm are undesirable. Nevertheless, work continued on handling and processing the powder while working with the vendors to improve purity levels.

Particle size and distribution were also measured for each powder. Crystallite size was determined by x-ray line broadening; the results are summarized in the left column of Table 2. The conventional powder was observed to have a contribution to line broadening from a small volume fraction of powder with a nanoscale crystallite size. This was confirmed with subsequent testing using an ultrasonic particle size analysis unit (Matec Applied Sciences). Typical particle size distributions are summarized in Figure 10.

Table 2: Powder characterization summary

Yttria Source	Crystallite Size (nm)	Primary Agglom. Size (nm)	Major Impurities
Conv-1	55	5 μm + fines	
Nano-1	40	118	B, Na, Mg, Al, Si (22.5x), P, S, Cl, K, Ca, Fe, Ce
Nano-2	11	130	B, Si (14x), S, Cl
Nano-3	13	140 + coarse	B, Na, S, Si (2.1x), Cl, Ca, Zn, Ce

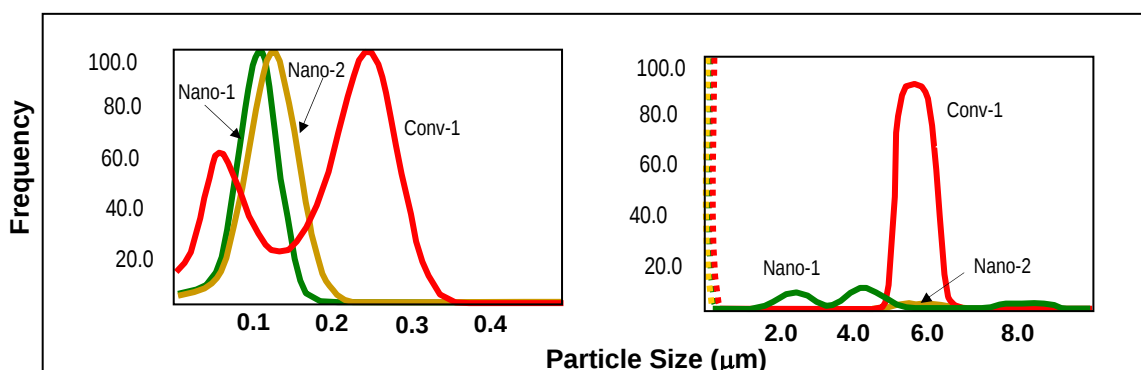


Figure 10: Particle size distribution of the powders investigated.

Since the calcination step of the Nano-3 process causes significant agglomeration, it was necessary to ball mill that powder for several hours prior to the particle size measurements. The Nano-3 yttria exhibits a major peak centered at approximately 140 nm. Two additional peaks at approximately 4.0 and 8.5 μm clearly demonstrate that the milling and sonication treatments did not fully disperse the material. Although the 140 nm particles are great in number, they contributed only approximately 20% of the volume in this slurry.

The Nano-1 and Nano-2 powders exhibit strong maxima at 118 and 130 nm respectively, in the same range as the principal peak of the Nano-3 yttria. The Nano-1 material has agglomerates of approximately 2.5 and 4.0 μm , evidence of incomplete dispersion. The Nano-2 powder is the best dispersed of the nano-yttrias, although a small contribution due to 6 μm agglomerates can be seen in the original plot.

Shrinkage studies were initiated with a Theta Industries Dilatronic IIR dilatometer using a single push rod LVDT. Shrinkages for both the conventional yttria powder and the nanopowders are shown in Figure 11.

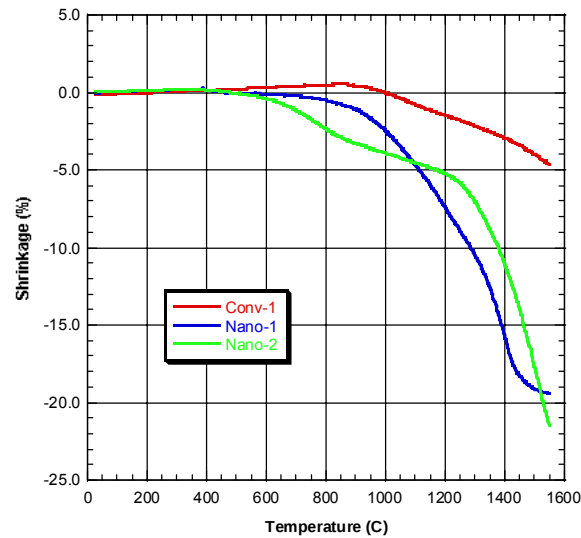


Figure 11: Initial shrinkage behavior for various yttria powder compacts.

The conventional Y_2O_3 powder showed a shrinkage onset temperature of 900°C . Compared to the nanoscale materials, the shrinkage progressed at a much slower pace. Total shrinkage for the Conv-1 material was 4.8 %. These results are consistent with previous experience, as conventional Y_2O_3 is typically sintered at $>1700^\circ\text{C}$ to attain a closed-pore state. The two nanopowders, on the other hand, exhibited substantial shrinkage under the conditions evaluated. The Nano-1 and Nano-2 materials exhibited onsets of shrinkage at approximately 700°C and 550°C , respectively. The fact that the Nano-2 material begins to densify at a lower temperature is consistent with the difference in primary crystallite size observed via x-ray diffraction. Additionally, there is a crossover point near 1400°C where the shrinkage of the Nano-2 material overtakes that of the Nano-1 material. Although the green density of the Nano-1 powder is higher (50 %TD as opposed to 40 %TD), this crossover phenomenon was observed in parallel experiments that directly measured the density of the sintered tablets.

Sinter + HIP processing also performed on all three nanoscale materials to investigate the effects of the impurity levels on transparency. Samples of Conv-1, Nano-1, and Nano-2 material were pressed to 60, 50, and 40 %TD respectively. The compacts were sintered at 1650°C in air for 4 hours, and then HIPed at 1650°C for 4 hours under 29 kpsi. The Nano-1 material was measured to be 100.0 %TD and was quite transparent although possessing a yellow color, probably due to substantial Ce impurities. The Nano-2 material was modestly transparent, and was also observed to have a bulk density of 100.0 %TD, but had many small cracks and fissures that decreased the apparent density to 98.4 %TD. These defects were probably the result of differential shrinkage caused by density gradients in the green tablets, and would be expected to be eliminated with an optimized green body forming process. In addition to the fissures, there were dark, opaque inclusions distributed heterogeneously throughout the bulk of the sample, attributed to precipitated phases consisting of the various impurities present. Annealing the sample resulted in no apparent increase in transparency. Figure 12 shows the transparency for the Nano-1 and Nano-2 samples.



Figure 12: Translucent yttria disks. Left: Made from Nano-1 powder (0.9 mm thick). Right: Made from Nano-2 powder (2.0 mm thick).

The Nano-3 material was also processed using this approach, but only reached 95.3 %TD with no transparency. This result indicates that this material probably did not reach closed pore density during the sintering step, and a higher temperature would be required to process it to full density, which could be incompatible with the goal of limiting the grain growth.

Compared to conventional yttria powder, the sinterability of all of the examined nanopowders proved superior, as expected. Green compacts were sintered to a closed pore state at temperatures as low as 1400°C, and with soak times as short as 12 minutes at 1550°C. Nano-2, the most active nanopowder, could only be compacted to a green density of 40 %TD. Besides obtaining purity goals, improved green consolidation is the remaining key technology to capture to prepare transparent, nanograined yttria.

Current transparent nano-yttria fabrication efforts address the issues revealed in initial studies as noted above. Continued work with powder suppliers has led to higher purity starting materials. Additional sources of yttria nanopowder have also been identified, including an in-house processing route. Elimination of impurities will allow single phase materials with low absorption and scattering to be fabricated. Consolidation of these powders is being improved through wet processing techniques. Optimization of both suspension rheology and forming processes will produce compacts with high green density. In addition, optimization of the firing schedule utilized to bring the compacts to a closed-pore state prior to HIPing is being investigated in order to minimize grain growth and produce fine-grained transparent yttria ceramics with improved strength and thermal shock resistance.

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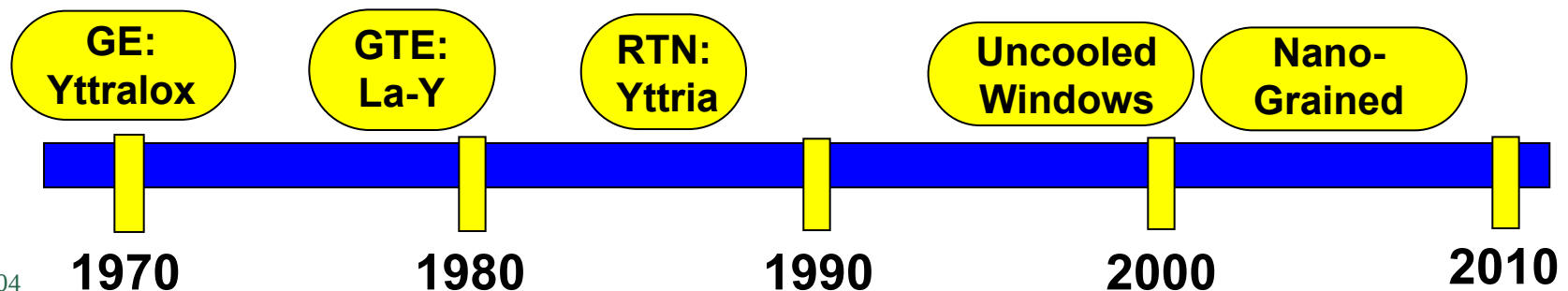
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10th DoD EM Windows Symposium
May 19, 2004

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- Nano-grained Yttria Development (2002 →)

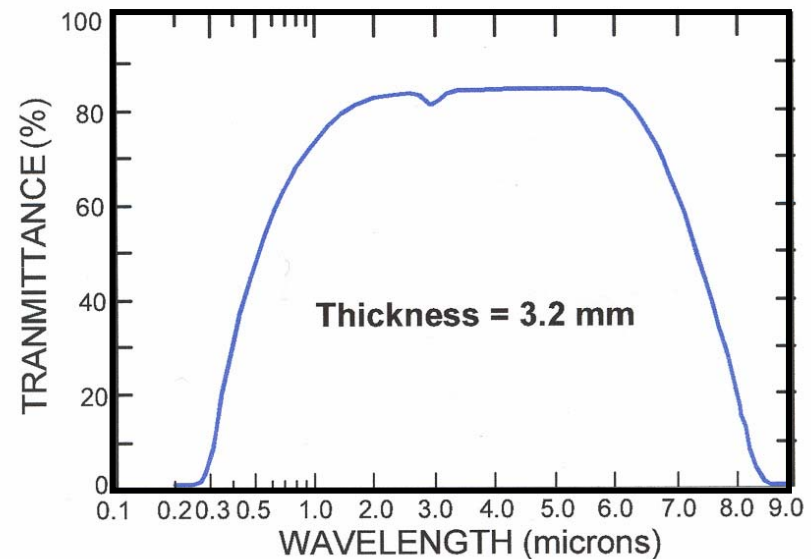
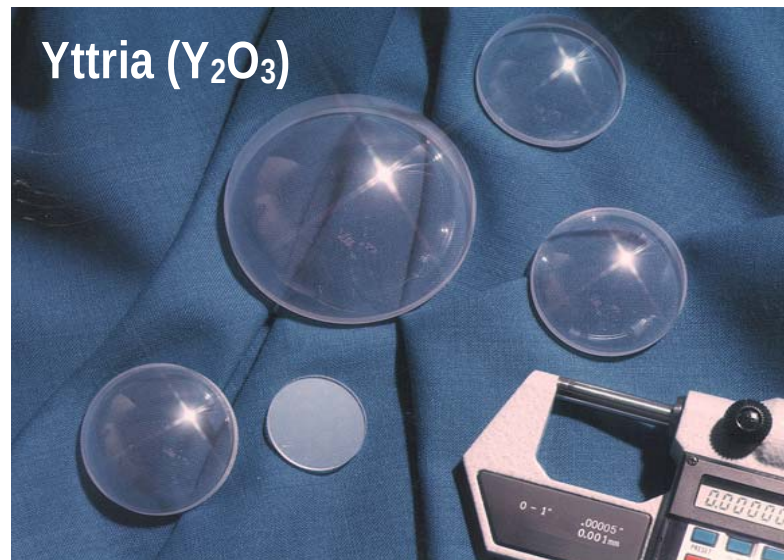


Background

- Yttrium Oxide (Y_2O_3 – yttria) has excellent optical properties in the visible, NIR, and the full 3-5 μm MWIR band
- Transparent yttria ceramics have been produced with high optical quality and tested as windows and domes
- Conventional yttria (with grain sizes $\geq 100 \mu\text{m}$) has ~150 MPa (~20 kpsi) fracture strength
- Substantial strengthening ($\geq 2\text{X}$) will enable many additional DoD applications

RAYTRAN Transparent Yttria

Raytheon
Integrated Defense Systems

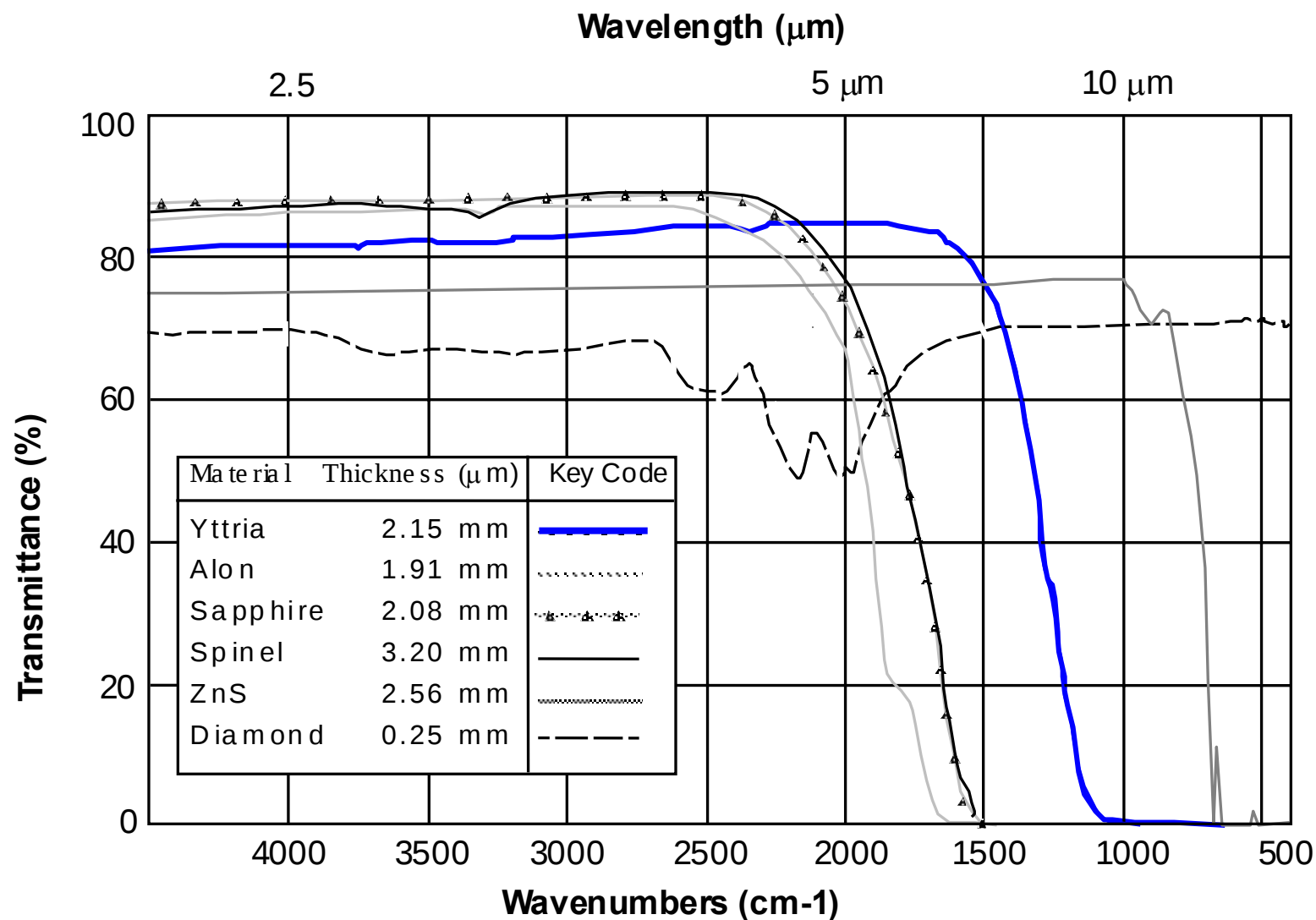


Typical Properties of Raytran® Yttria

Composition	Y ₂ O ₃	Poisson's Ratio	0.29
Density (gm/cc)	5.03	Thermal Expansion (30-200°C)	5.8 x 10 ⁻⁶ /°C
Grain Size (typical)	150 microns	Thermal Conductivity (25°C, cgs)	0.035
Flexural Strength (biaxial)	18,000 psi	Transmission Limits (microns)	0.25 to 8.5
Young's Modulus	24 x 10 ⁶ psi	Refractive Index (4μm)	1.89
Hardness (Knoop, 200g)	650 Kg/mm ²	Melting Point	2450°C

Yttria Provides Performance Advantages Over Sapphire and Other MWIR Materials

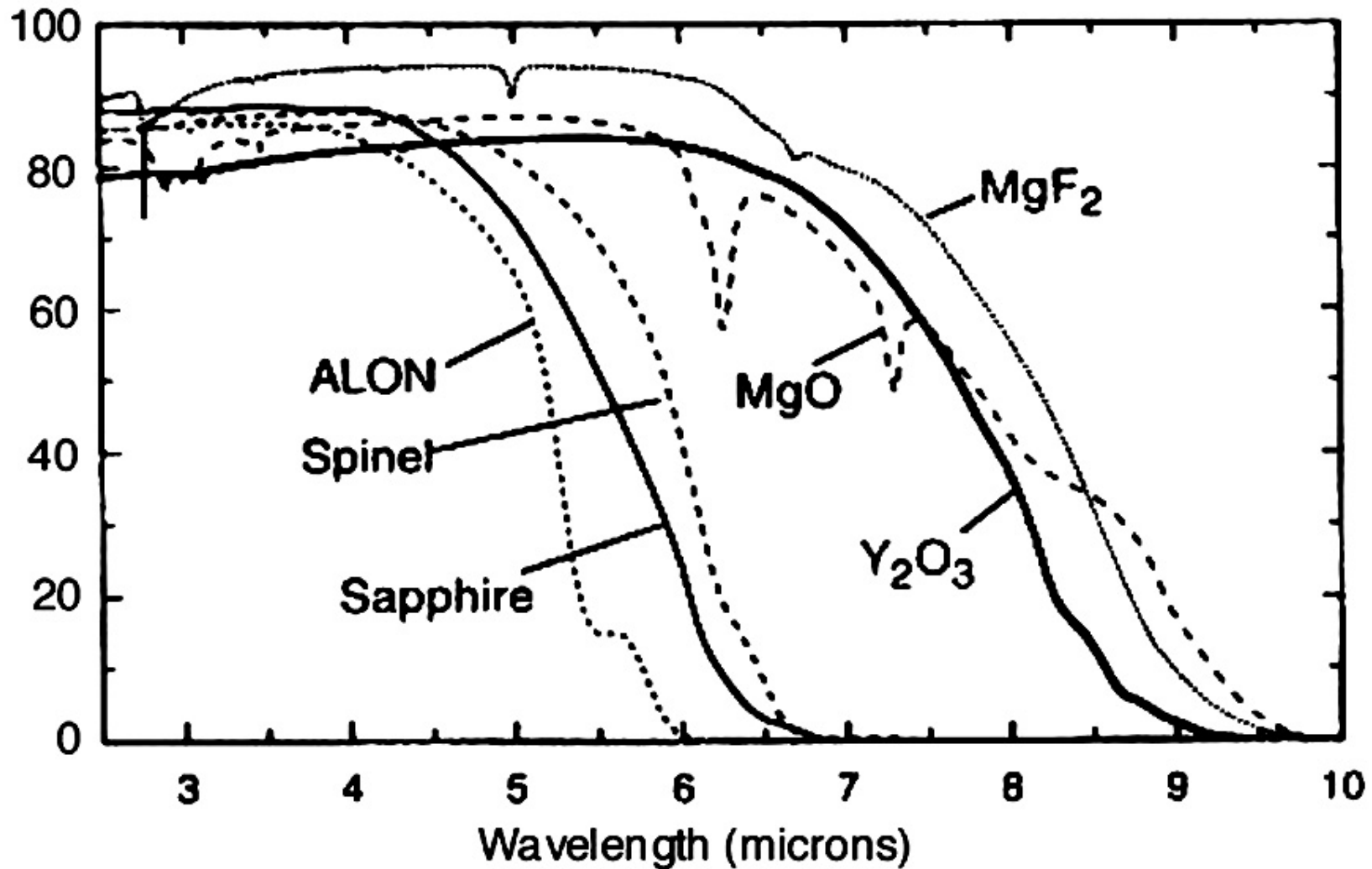
Yttria and other MWIR Materials – Transmittance



PBN-90-1768

Yttria and other MWIR Materials – Transmittance

Raytheon
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Yttria Fracture Strengths

Temperature	# Samples	Average Strength
RT	18	22,500 psi (CV=32%)
300 °C	10	19,800 psi (CV=23%)
600 °C	18	17,700 psi (CV=27%)

CV is Coefficient of Variation
(standard deviation/ average)

Yttria and other MWIR Materials

Property	Units	ALON	Sapphire	Spinel	PSZ	Yttria
Refractive Index	(--)	1.75	1.75	1.75	2.15	1.95
IR Cut-off ($\beta=1 \text{ cm}^{-1}$)	(μm)	4.6	5.0	5.3	6.0	7.0
Flexural Strength	(MPa)	300	400	190	1400	160
Fracture Toughness	($\text{MPa}\cdot\text{m}^{1/2}$)	1.4	2.0	1.9	~5	0.7
Young's Modulus	(GPa)	88	340	131	180	70
Hardness	(GPa)	180	220	160	130	71
Thermal Conductivity	(W/m-K)	13	36	15	3	14
Thermal Expansion	(ppm/K)	5.8	5.3	5.6	9.0	6.6
Poisson's Ratio	(--)	0.24	0.27	0.26	0.30	0.30

MWIR Material Trade-offs

	Long Wavelength Cutoff*	Low Scatter	Durability	High Temp Stability	Optical Isotropy	Machinability
Yttria						
Sapphire						
Magnesia						
Zirconia						
ALON						
Spinel						



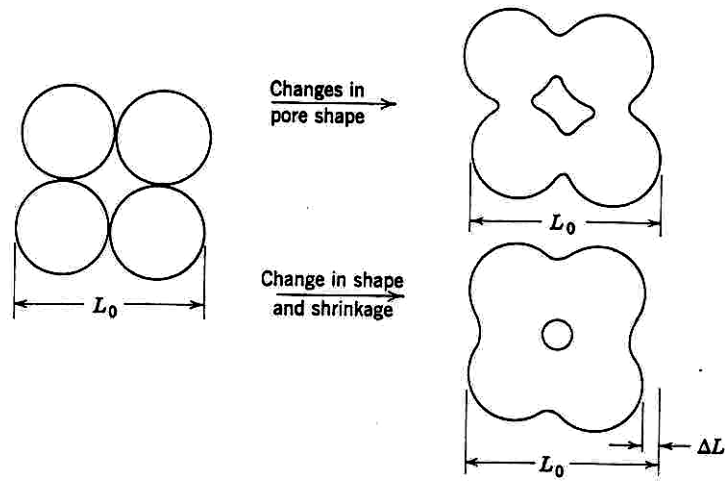
Excellent



Marginal

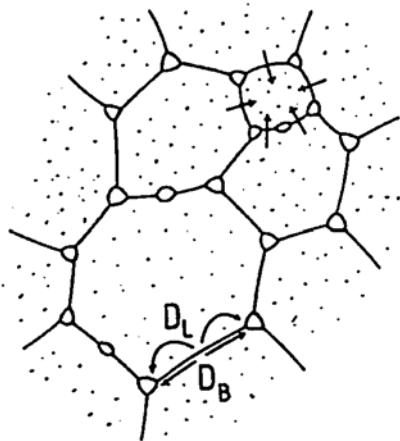


Poor



At High Temperatures:

- Porosity reduced (to a few percent)
- Via atomic diffusion
- Part shrinks (15-20% linear shrinkage)
- Grains grow in size
- Part geometry unchanged

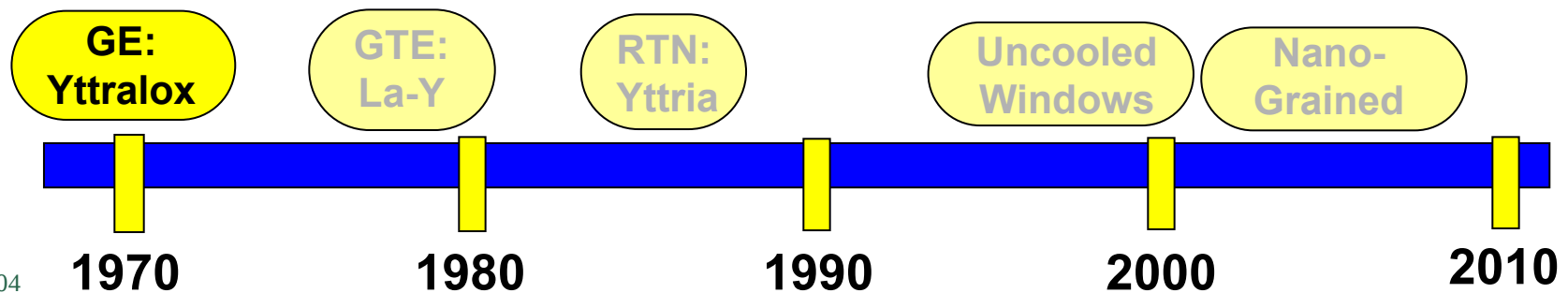


Driving Force:

- Reduce surface Energy
- Reduce surface & grain boundary Area
- Shrinkage happens rapidly at elevated temperature
- Applied pressure (Hot Press or HIP) provides additional driving force

Yttralox by General Electric

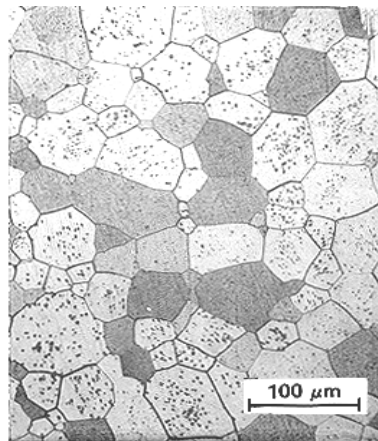
- Developed ~1970 by Chuck Greskovich et al. at GE
- Contained ~10% ThO₂ – to retard grain growth during sintering
- Sintered at >2000°C
- Applications:
 - Lighting
 - Ceramic Lasers



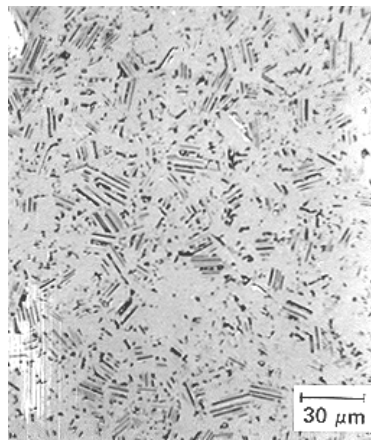
Transient Second-Phase Sintering

Raytheon
Integrated Defense Systems

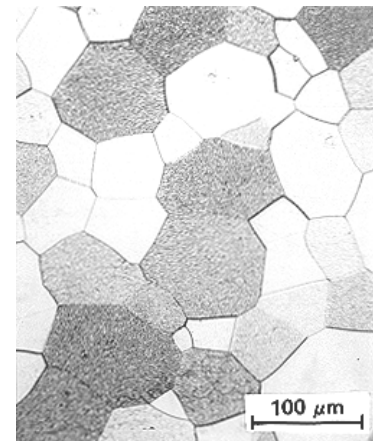
Yttria Sintering



As Sintered

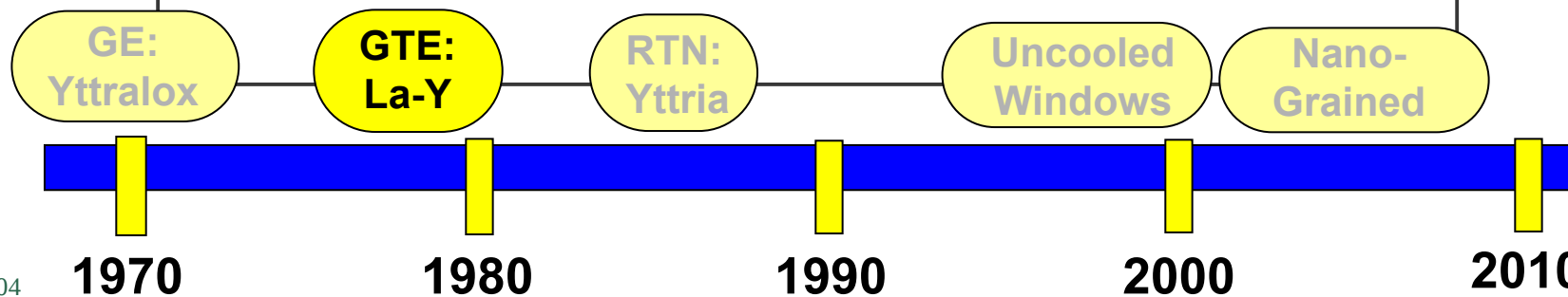


As Sintered



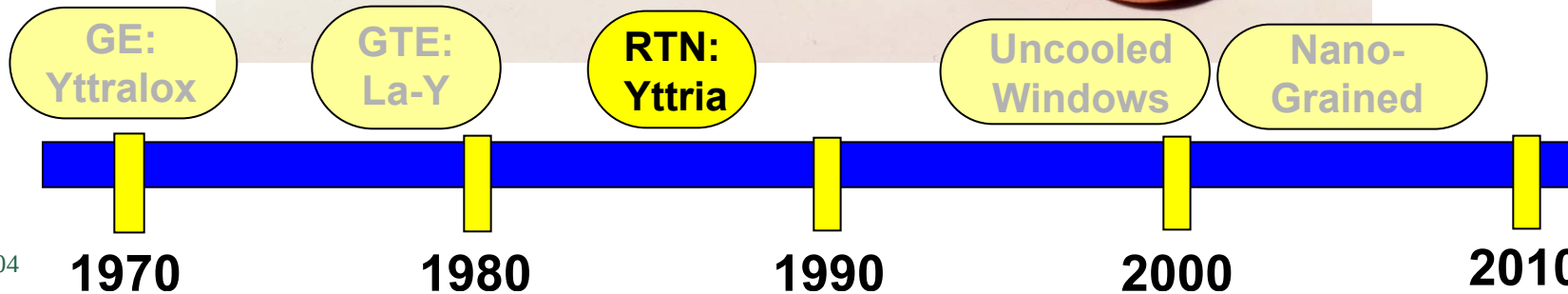
Sinter-Annealed

Developed by Bill Rhodes at GTE Labs.



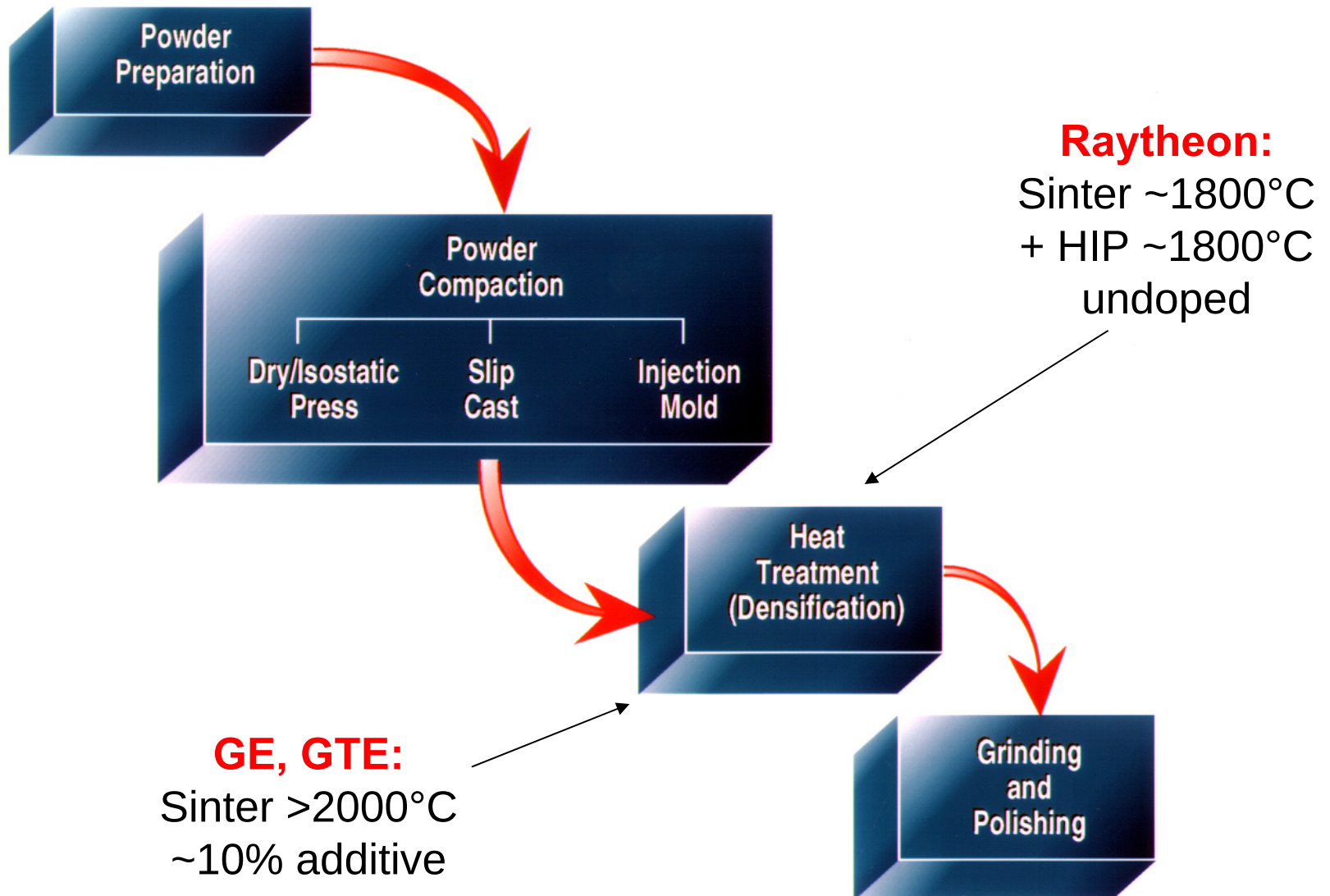
Undoped Yttria Dome

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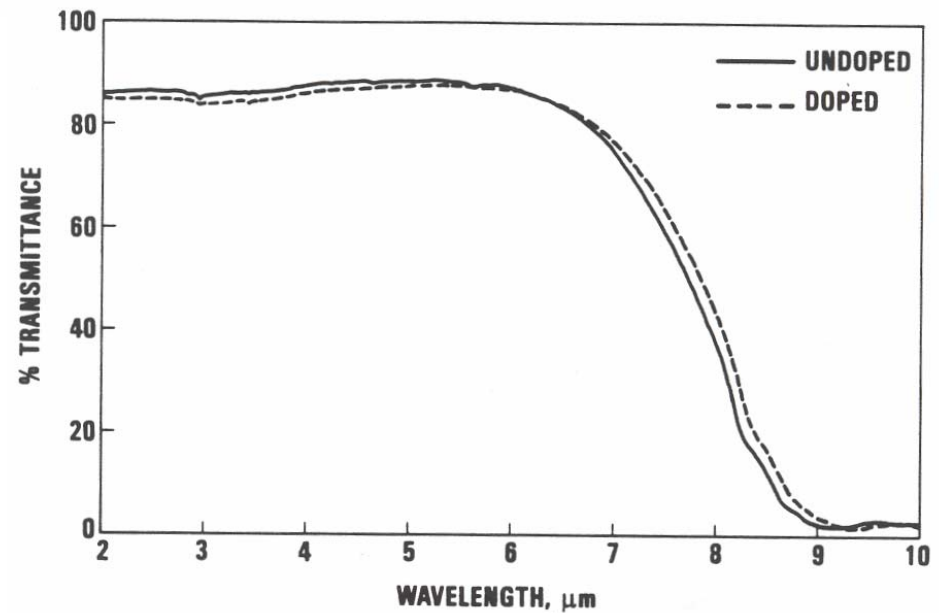
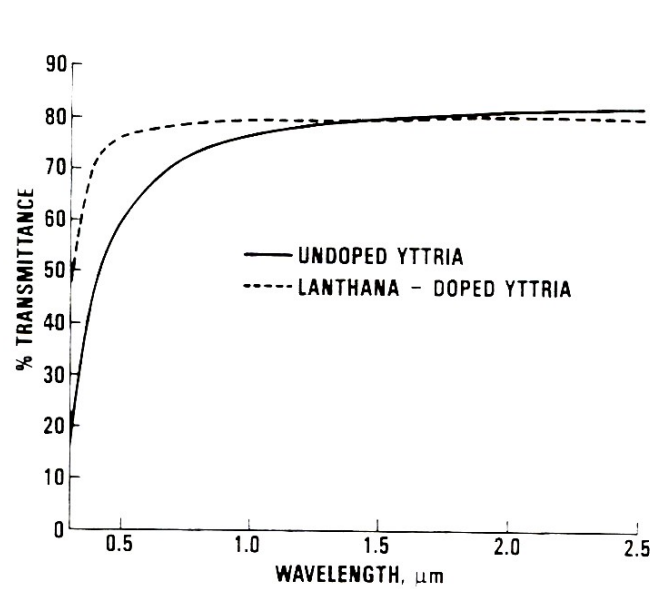
Y_2O_3 Window Fabrication

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Previous Yttria Development – Optical Transmittance

Raytheon
Integrated Defense Systems



Raytheon undoped Yttria and GTE La-doped Yttria extensively characterized by Naval Weapons Center

From NWC TP 7002

Previous Yttria Development – Mechanical Properties

NWC TP 7002

TABLE 29. Summary of Mechanical Properties at Room Temperature.

Property	Undoped yttria	Lanthana-doped yttria
Poisson's ratio	0.30	0.30
Uniaxial flexure strength ^a	10.8 Ksi ^b	14.3 Ksi
Equibiaxial flexure strength ^c	16.8 Ksi	23.7 Ksi
Flexural modulus ^a	23.5 Msi ^d	22.0 Msi
Compressive modulus ^e	27.8 Msi	25.8 Msi
Tensile modulus	25.3 Msi	24.4 Msi
Young's modulus ^f	24.2 Msi	24.1 Msi ^g
Shear modulus	...	9.3 Msi
Bulk modulus	...	20.8 Msi

^a From Tables 24 and 25.

^b Ksi = 10³ lb/in².

^c From Tables 26 and 27.

^d Msi = 10⁶ lb/in².

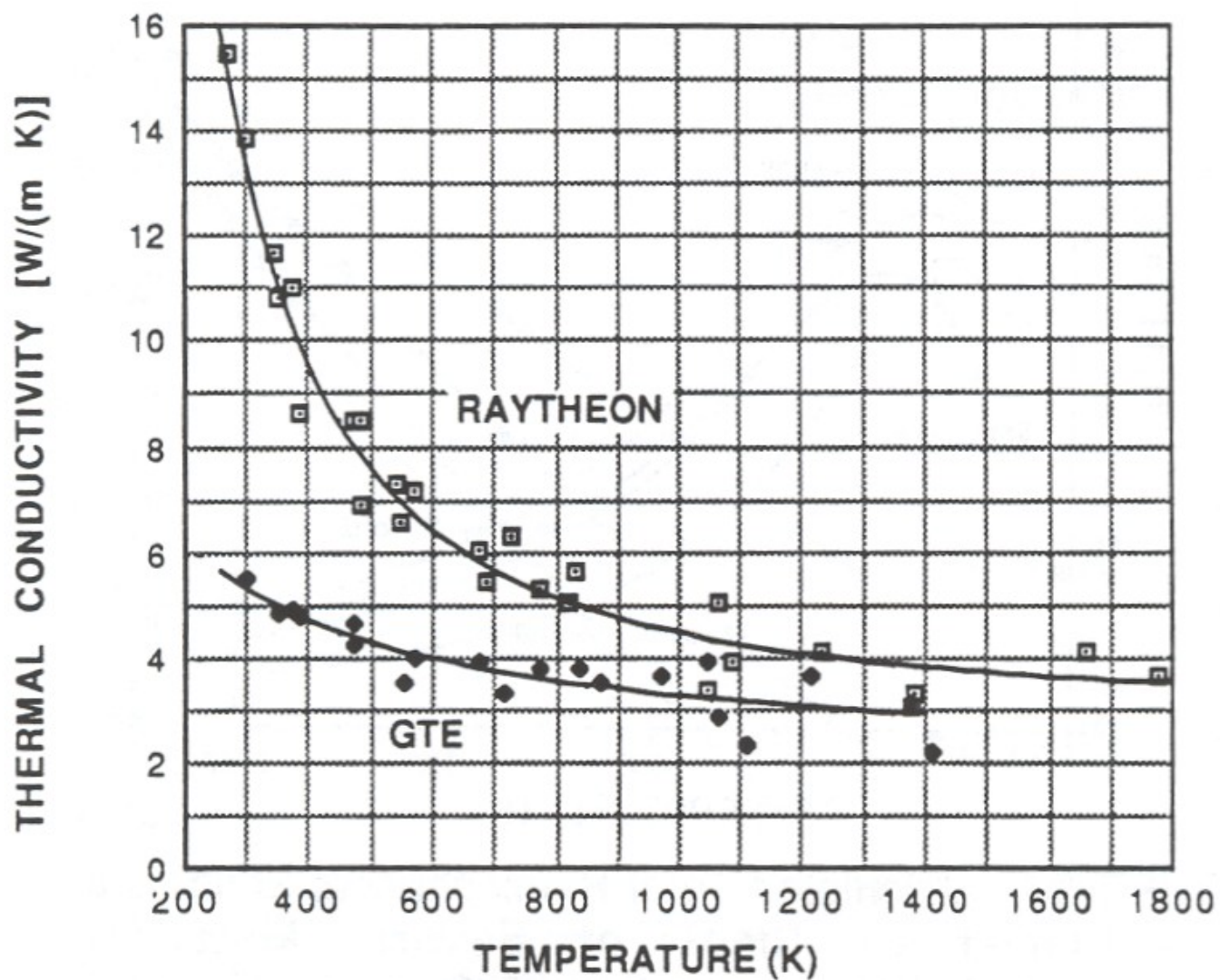
^e From Table 28.

^f Sonic modulus.

^g Average of values from GTE and Southern Research Institute.

Previous Yttria Development – Thermal Conductivity

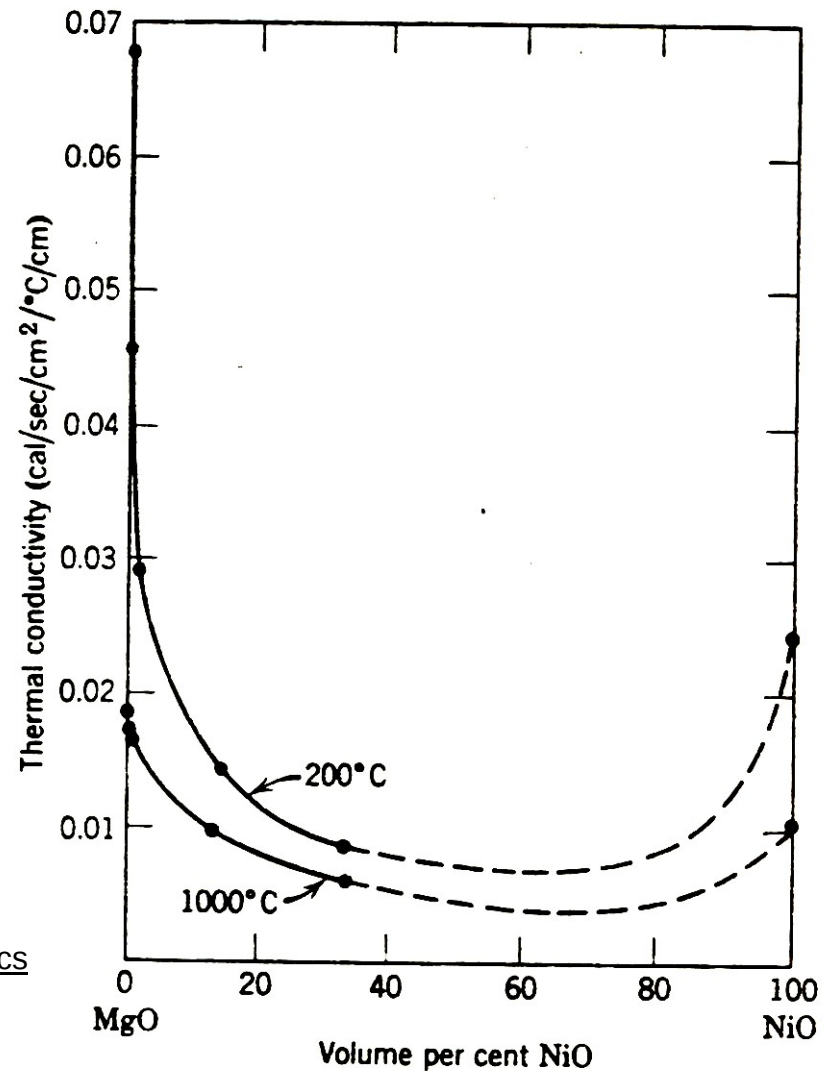
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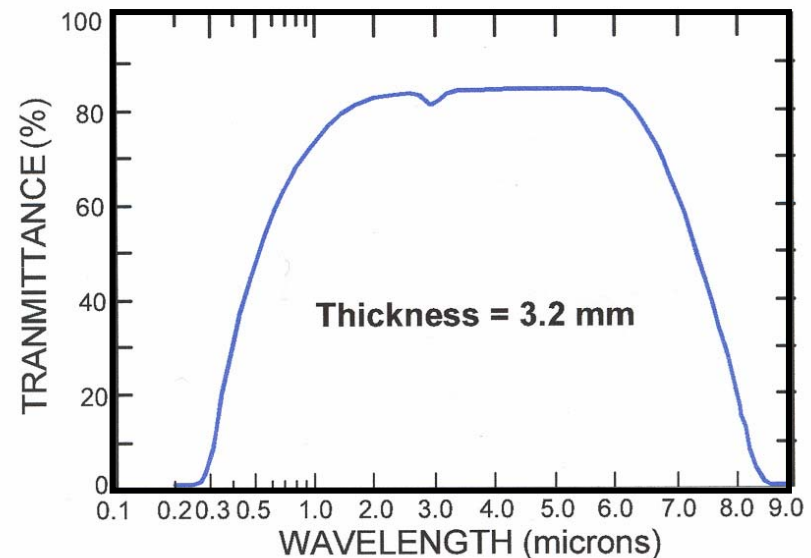
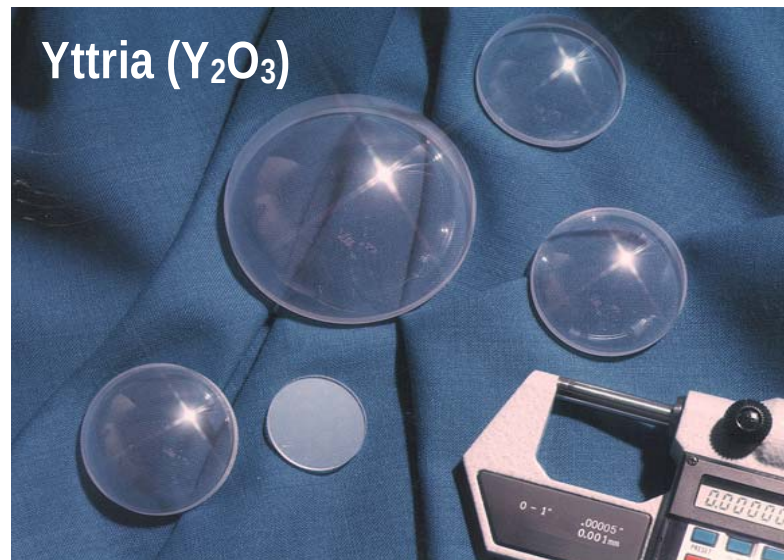
From NWC TP 7002

Thermal Conductivity

- Highest in simple, high purity crystalline oxides
- Substantially reduced by small amounts of additives



From Kingery, Introduction to Ceramics



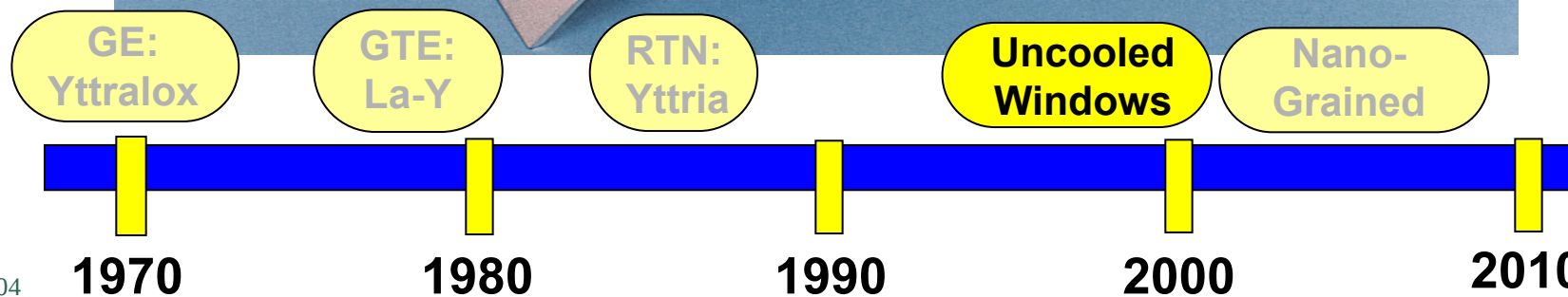
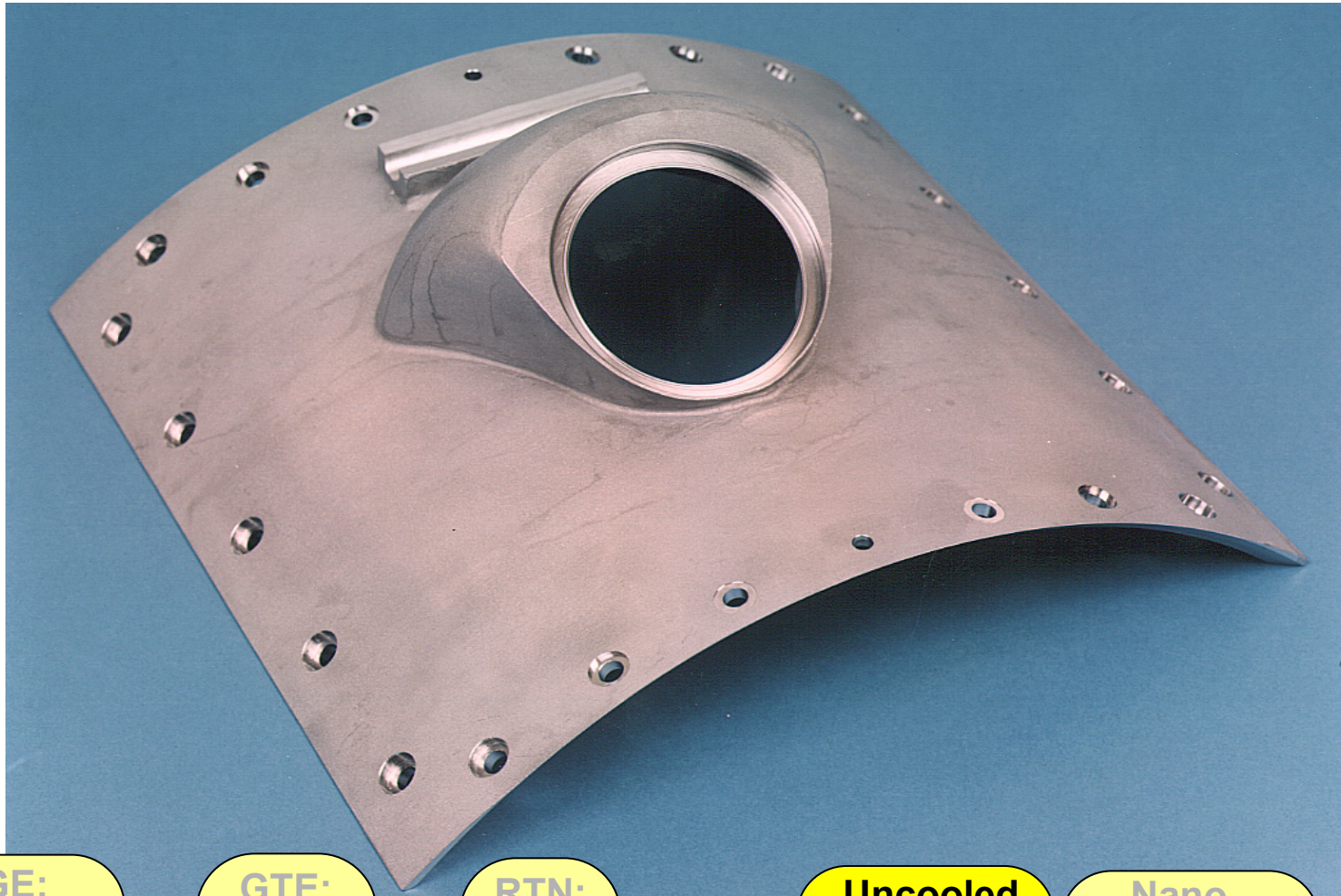
Typical Properties of Raytran® Yttria

Composition	Y_2O_3	Poisson's Ratio	0.29
Density (gm/cc)	5.03	Thermal Expansion (30-200°C)	$5.8 \times 10^{-6}/^{\circ}C$
Grain Size (typical)	150 microns	Thermal Conductivity (25°C, cgs)	0.035
Flexural Strength (biaxial)	18,000 psi	Transmission Limits (microns)	0.25 to 8.5
Young's Modulus	24×10^6 psi	Refractive Index (4 μ m)	1.89
Hardness (Knoop, 200g)	650 Kg/mm ²	Melting Point	2450°C

Conventional Yttria mature by 1985, but little interest until 2000

Uncooled Sidemount Flat IR Window

Raytheon
Integrated Defense Systems

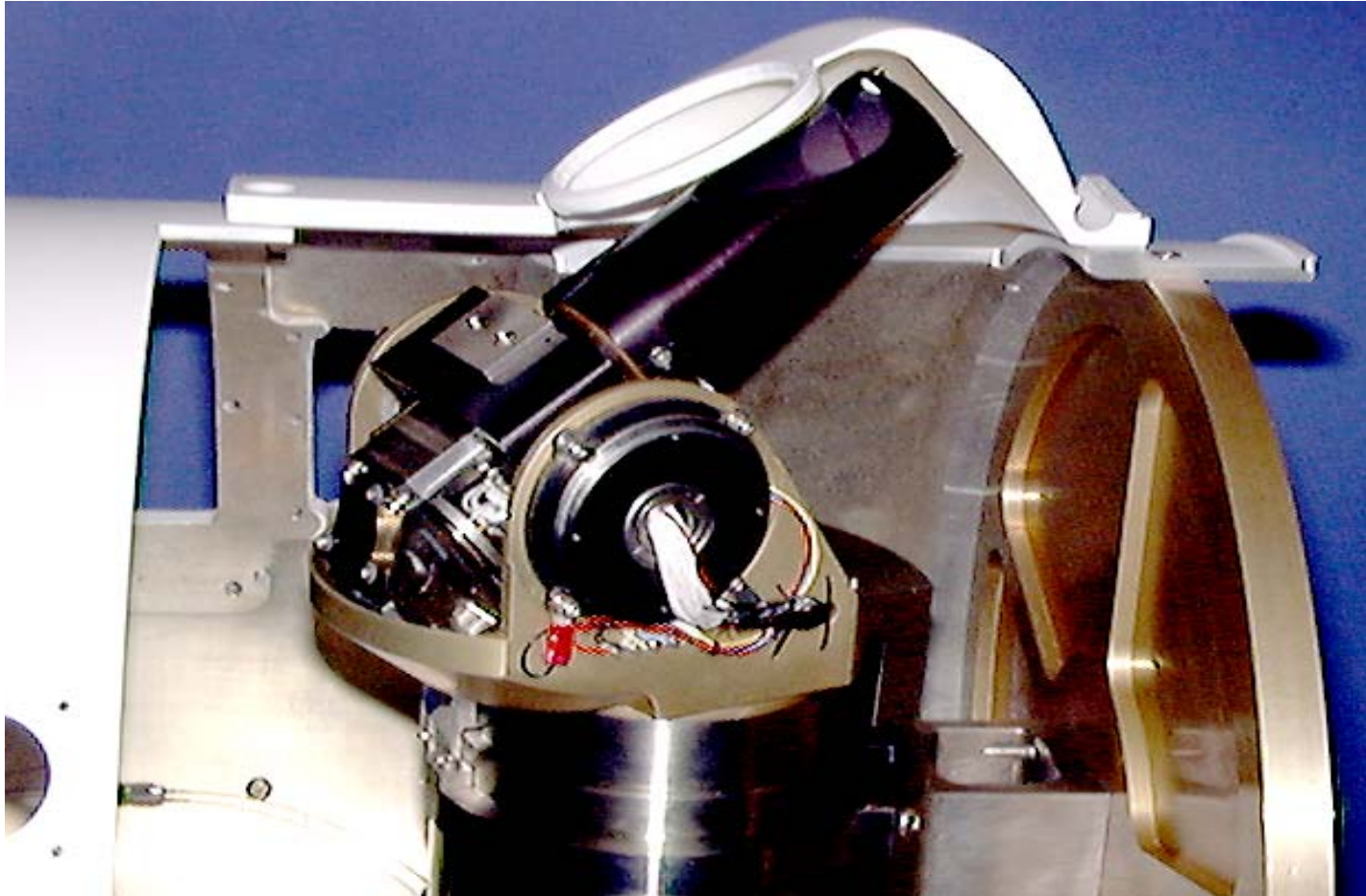


- **Eliminates Dome Cooling System**
 - Reduces system cost, weight, and qualification costs
- **Y₂O₃ window extends usable seeker bandwidth**
- **Increases engagement envelope to lower altitudes**
- **Meets or exceeds all key performance parameters**



Sidemount Seeker Prototype Built and Tested

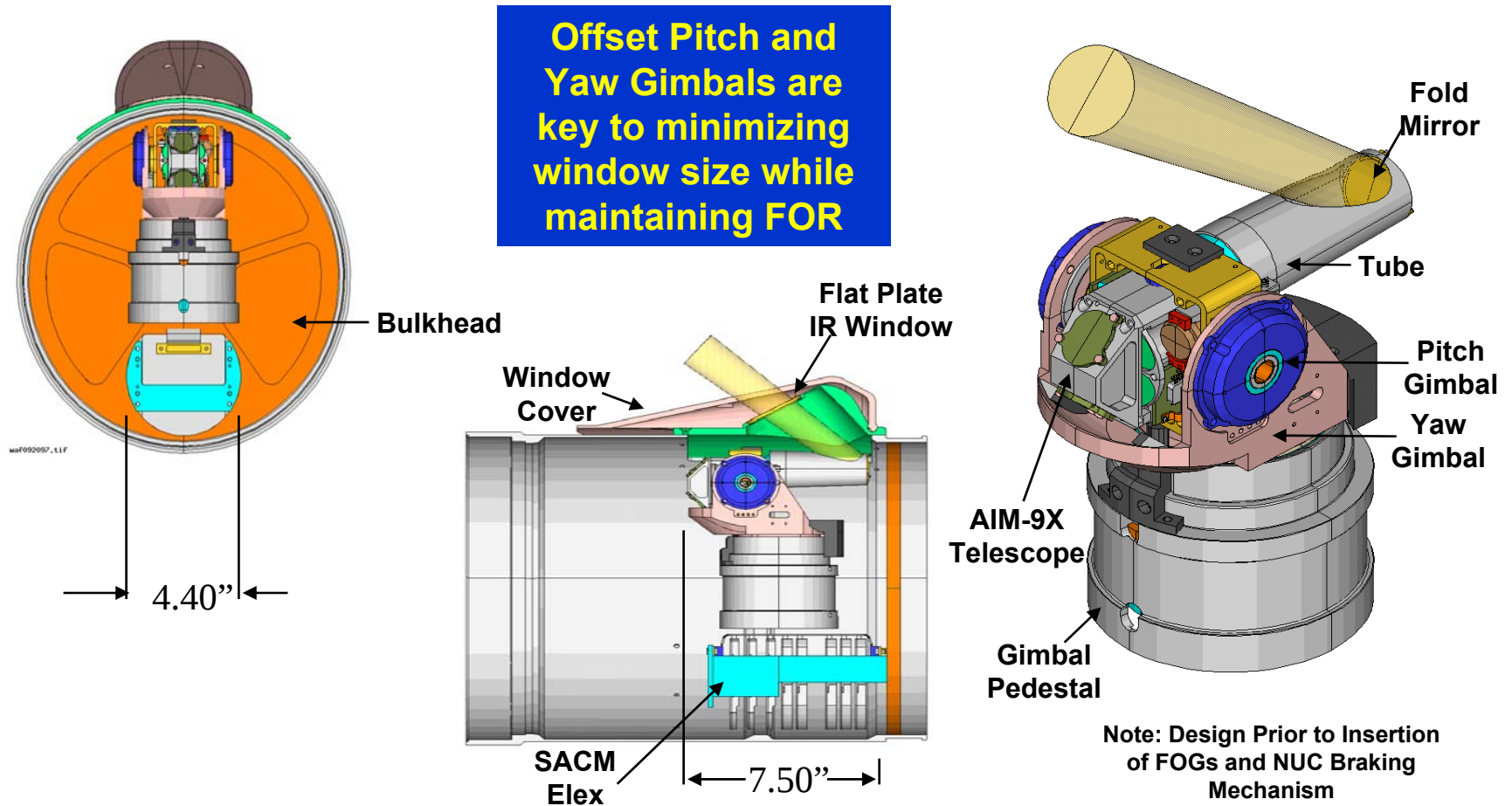
Raytheon
Integrated Defense Systems



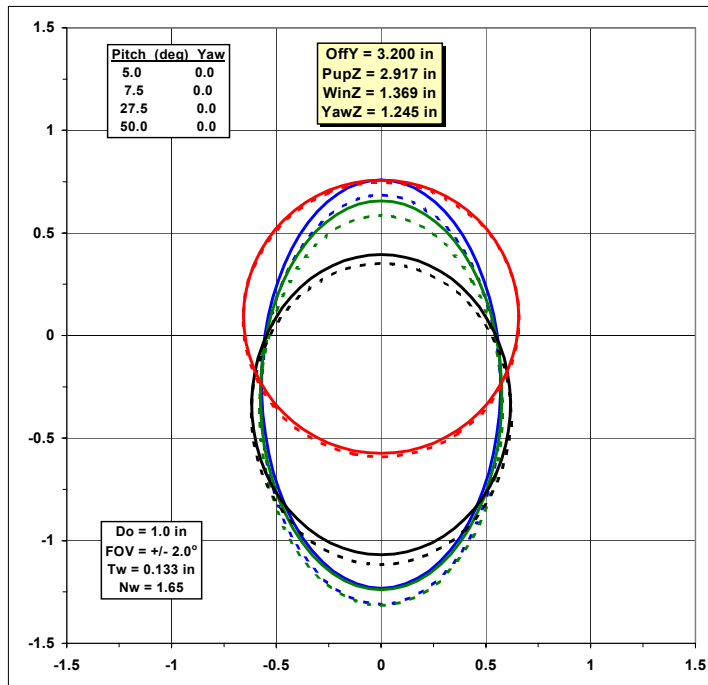
Compatible with established missile dome cover and guidance section

Seeker Meets Packaging Requirements

Raytheon
Integrated Defense Systems

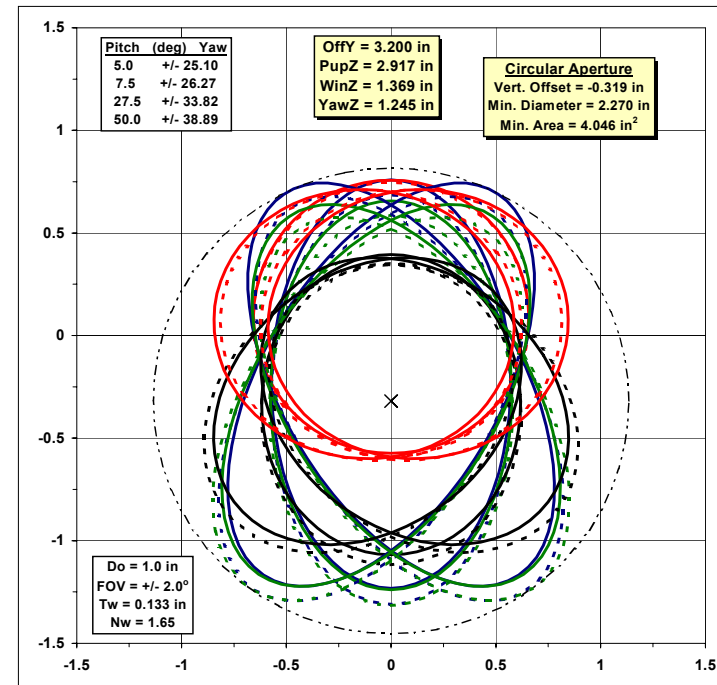


Rim Ray Projections on Flat Window



Pitch Angles Only

Required Height < 2.1 in.



Yaw and Pitch Angles

Required Diameter = 2.3 in.

Appropriate Pitch Axis Selection and Offset Yaw Axis Minimize Both the Window Aperture and "Beam" Motion over Window

Window Property Trades

Window Material Trades					
Material	Thermal Cond	CTE	Strength	dn/dT	LWIR Cutoff
Si	High	Low	Med	High	Med
ZnS	Low	Med	Med	Med	High
GaP	High	Med	Med	High	High (9 μ m abs)
MgO	Med	High	Med	Low	Med
Y ₂ O ₃	Low	Med	Med	Low	Med
Sapphire	Med	Med	High	Low	Low
ALON	Low	Med	High	Low	Low
MgF ₂	Low	High	Med	Low	Med
Diamond	V. High	Low	High	Low	High (MW abs)
Ge	Med	Med	Med	V. High	High
GaAs	High	Med	Low	High	High AIT-V088

High thermal cond. -> minimizes temperature gradients

Reduces stress and Wavefront distortion

Low CTE -> reduced stresses and wavefront distortion

High strength -> increased structural robustness

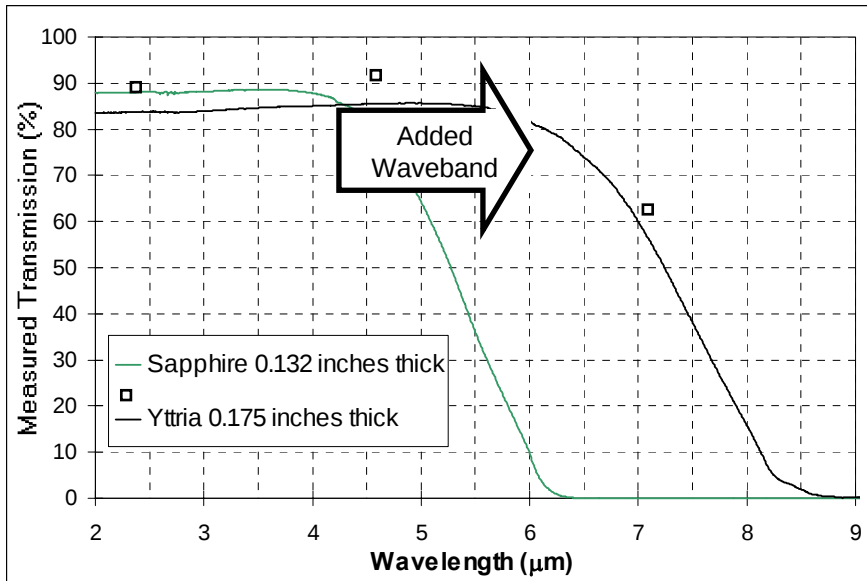
Low dn/dT -> reduced wavefront distortion

High LWIR cutoff -> expands available waveband range



2.37" dia. X 0.16" thick

Optical



- Larger usable waveband for Yttria increases optical performance
- Added waveband of Yttria relative to sapphire gives
 - 16dB higher S/N at uncover
 - 7dB higher S/N at nominal in flight condition
 - 14dB lower sensitivity to solar scatter and clutter

Mechanical

Measured Yttria Strengths

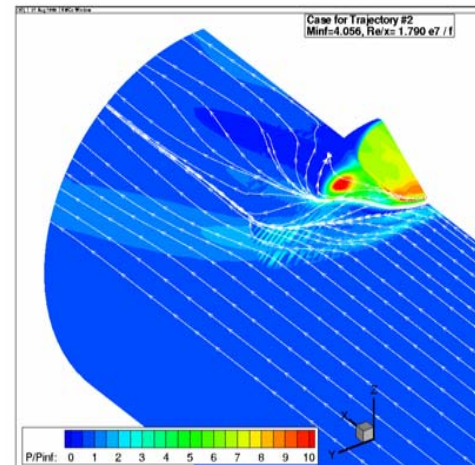
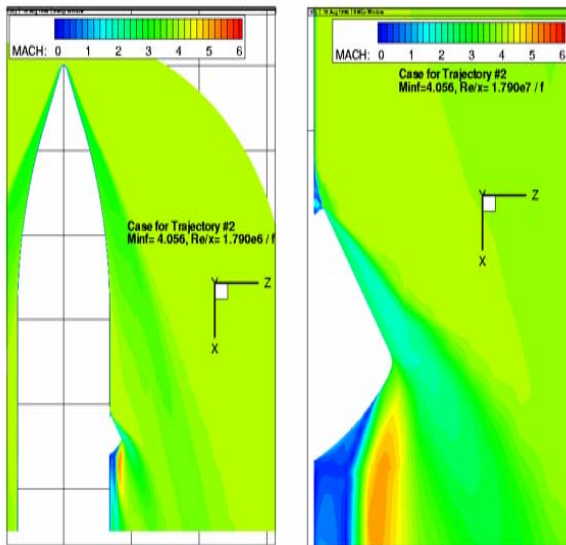
Temperature	# Samples	Average Strength
RT	18	22,500 psi (CV=32%)
300°C	10	19,800 psi (CV=23%)
600°C	18	17,700 psi (CV=27%)

- Yttria strength meets current mission requirements

Yttria Provides Performance Advantages Over Sapphire and Other MWIR Materials

Computational Fluid Dynamics (CFD) Analysis

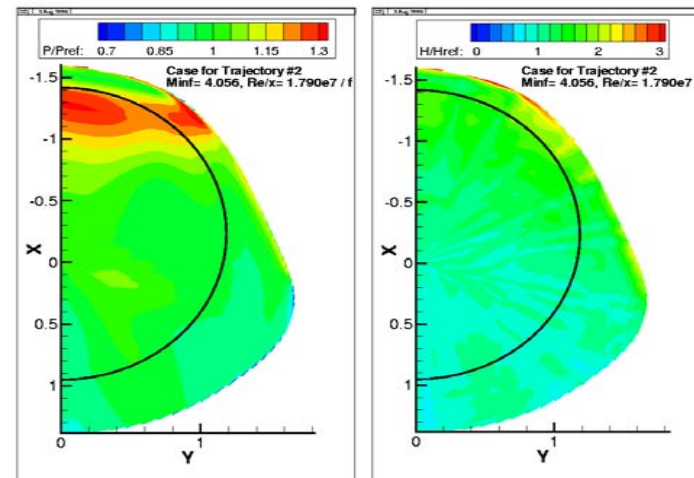
Raytheon
Integrated Defense Systems



- Housing shape effectively reduces window heating non-uniformity

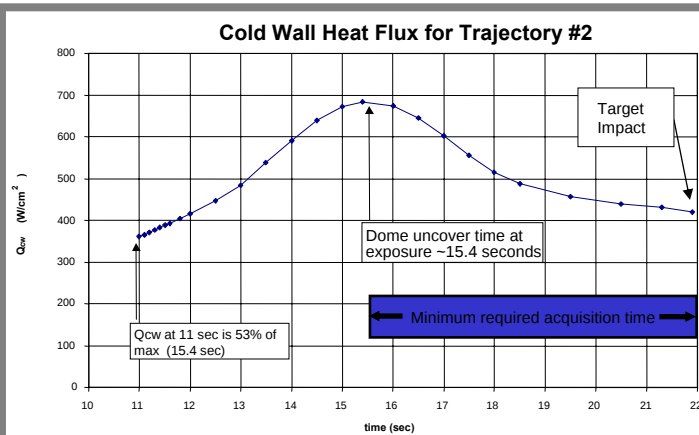
- Design driver trajectory is a low altitude intercept
 - Currently outside of performance envelope
 - Also analyzed high and mid altitude trajectories

**CFD analysis used to derive
aerothermal environment**

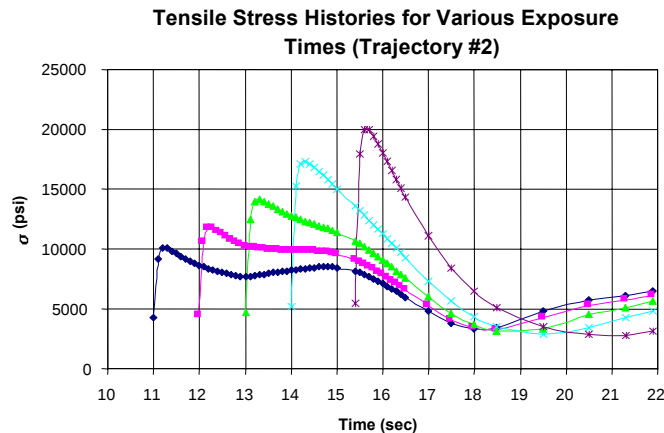


Flat Window Aerothermal Performance

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- Dome uncover is at last point before minimum acquisition range
 - Occurs at time of peak heating
 - Would maximize stress for flat window



- Flat window can be uncovered earlier with no penalty
 - Significant structural advantage

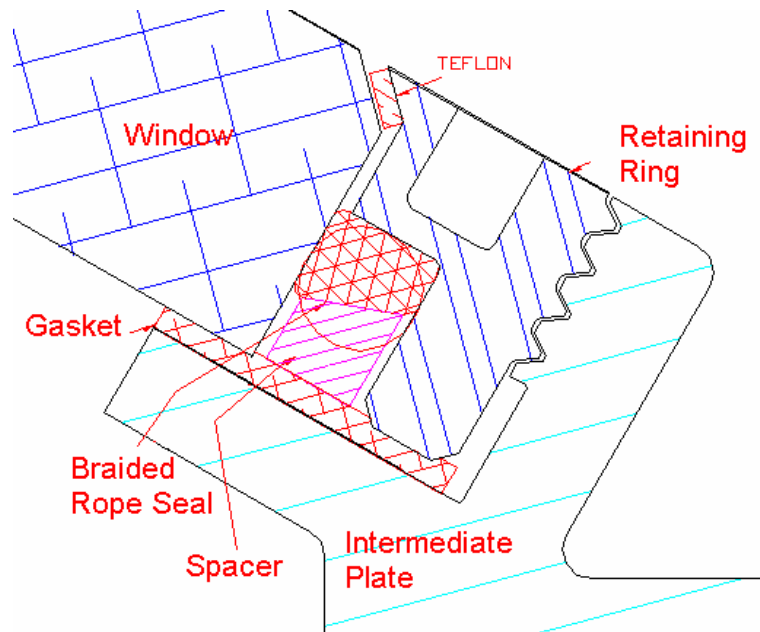


- Flat windows are not self constrained
 - Decreased stress relative to domes which are self constrained
- Surface stresses are compressive for flat windows
 - Ideal for polycrystalline ceramics

- Flat window structural advantages
 - Stress decreases with time of exposure
 - Uncovering earlier decreases peak stress

Seals and Hardware Meet Design Goals

- Seal design survives the severe aerothermal loading of the test environment.
- Housing and sealing proved robust through repeated assembly/disassembly sequences



Cross-section of seal



Assembly of window and seal



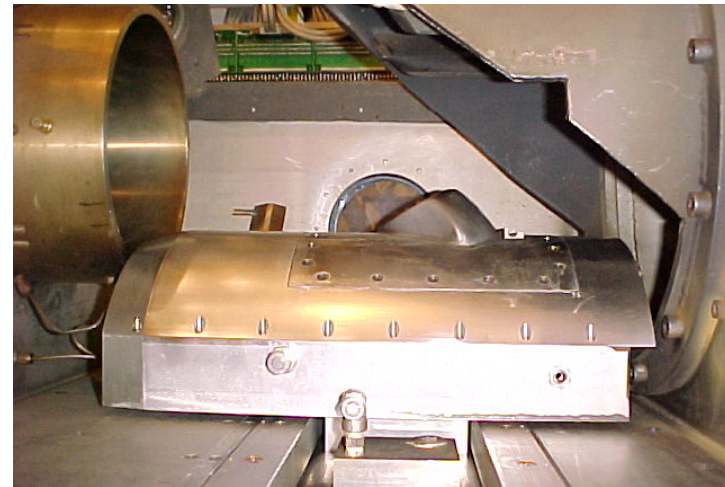
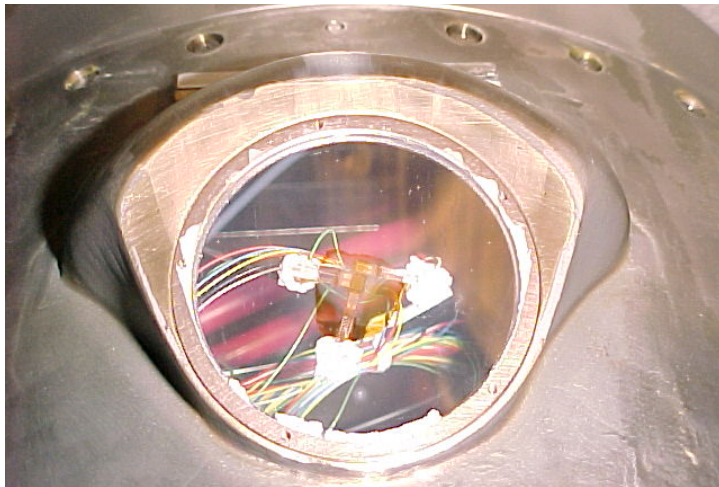
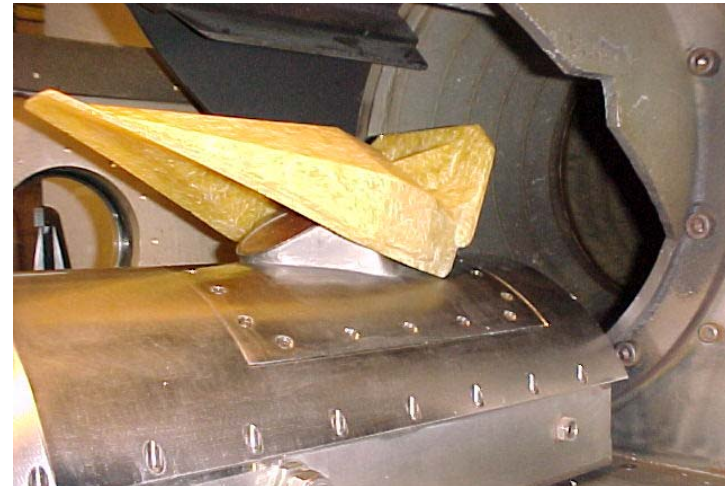
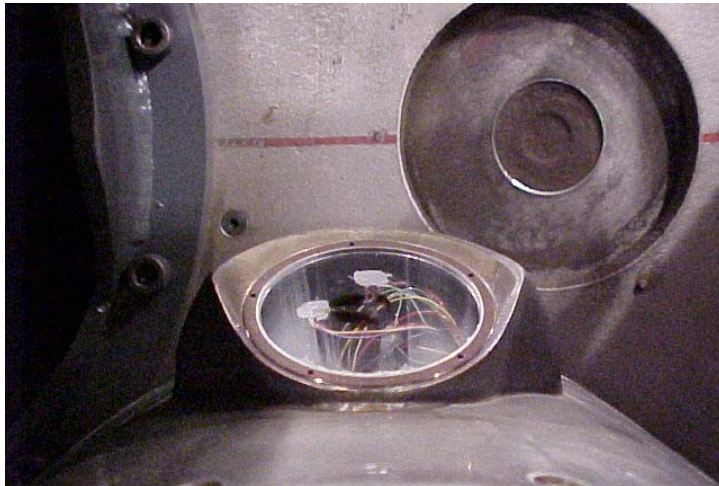
Intermediate plate is consistent with current missile design

Wind Tunnel Test Objectives

- Demonstrate uncooled flat yttria **window** structural robustness in severe aerothermal environment representative of missile flight conditions
 - Perform wind tunnel testing in common facility for close comparison with current cooled sapphire dome design (JHU/APL Cell # 4)
- Verify window seal performance
- Obtain detailed data on the window conditions in the aerothermal environment
- Validate window thermal structural models through comparison of instrumented data with analytical predictions

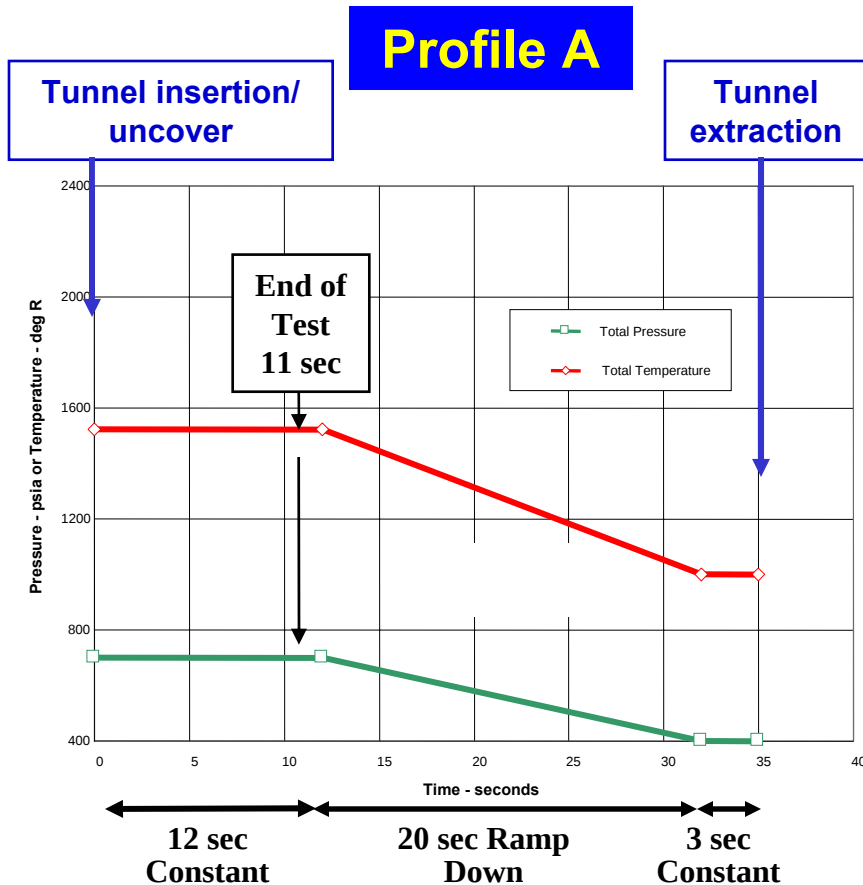
Flat Window Performance Validated Through Wind Tunnel Test

Raytheon
Integrated Defense Systems

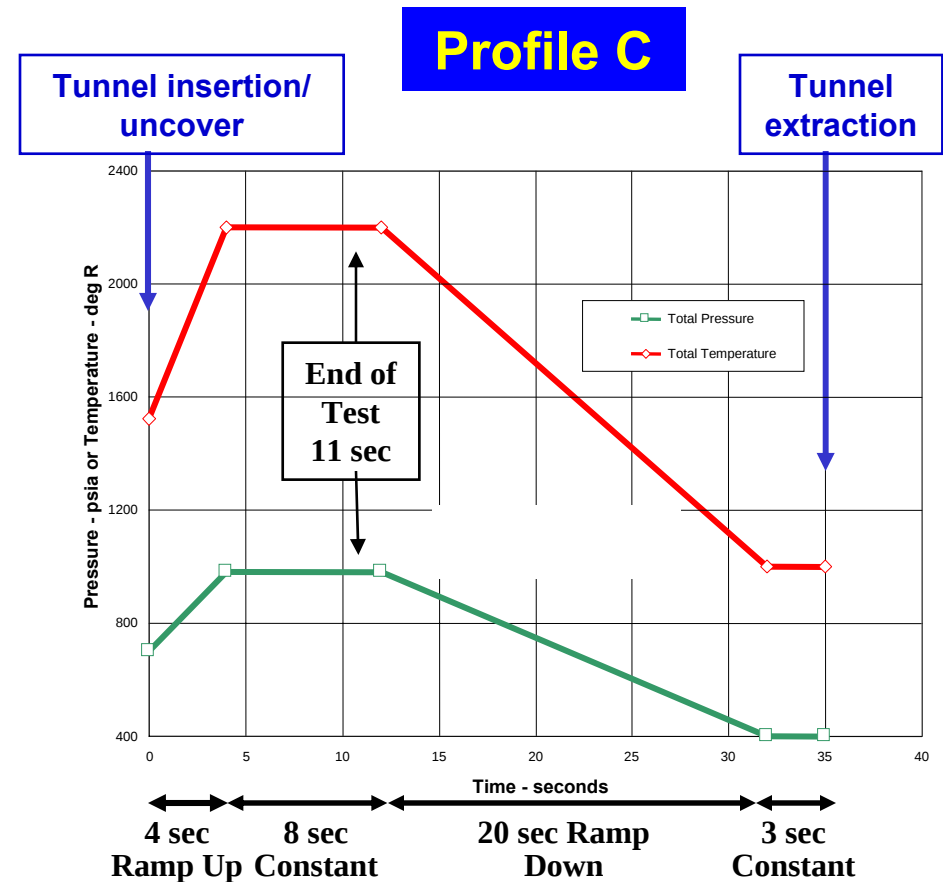


Wind Tunnel Heating Profiles

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Constant at $P_o=701$ psia, $T_o=1525$ R



Ramps from $P_o=701$ psia, $T_o=1525$ R
to $P_o=980$ psi, $T_o=2200$ R

**Hold state corresponds to missile flight conditions
Tunnel ramped to simulate driver trajectory (#2) heating**

Windows Test Results

- **First test used Profile A**

- Window survived without damage

- **Six windows tested at Profile C**

- 5 out of 6 windows survived testing undamaged
 - Window #83 remained intact through test
 - Crack formed at 6.5 seconds into test

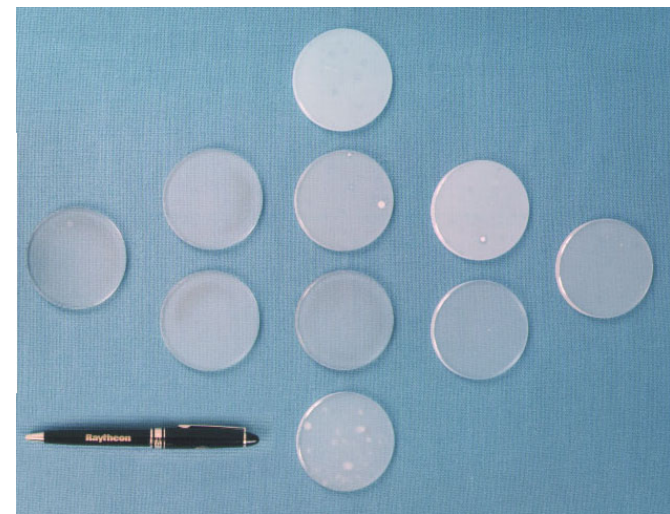
- **Window quality/ranking**

- Window quality was ranked before test (A to D)
Based on visual observations
 - Higher quality windows tested first
 - Window that cracked (#83) was C quality

- **Window mounted strain gauges and resistance temperature devices (RTDs)**

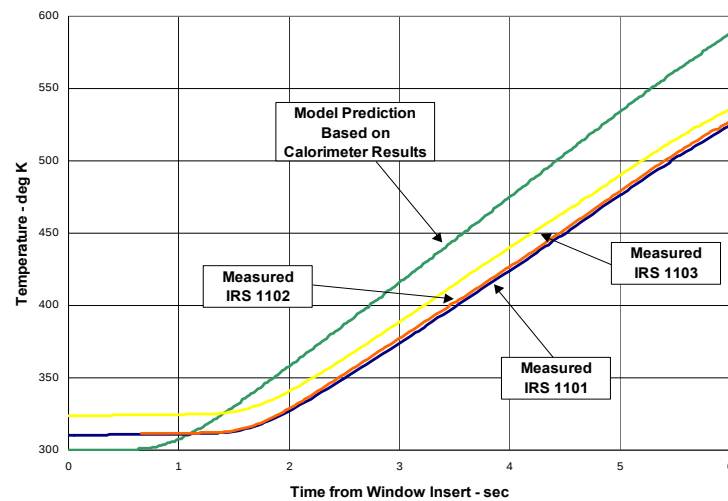
- Used to determine stresses
 - Validate thermal structural models

Test Order (run #)	Window #	Window Quality	Quality Ranking	Profile
1 (irs1099)	72	A	2	A
2 (irs1100)	80	A	3	C
3 (irs1101)	74	A	1	C
4 (irs1102)	70	C	4	C
5 (irs1103)	83	C	5	C
6 (irs1106)	34	C	6	C
7 (irs1107)	79	C	7	C



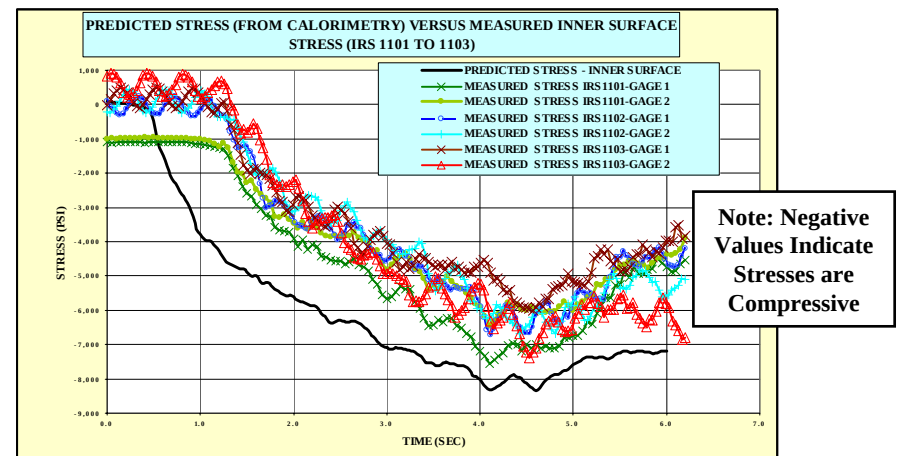
All Windows Retained Structural Integrity Throughout Test

Yttria Window Back Surface Temperatures - Profile C



Window Back Surface Temperatures Verify Model

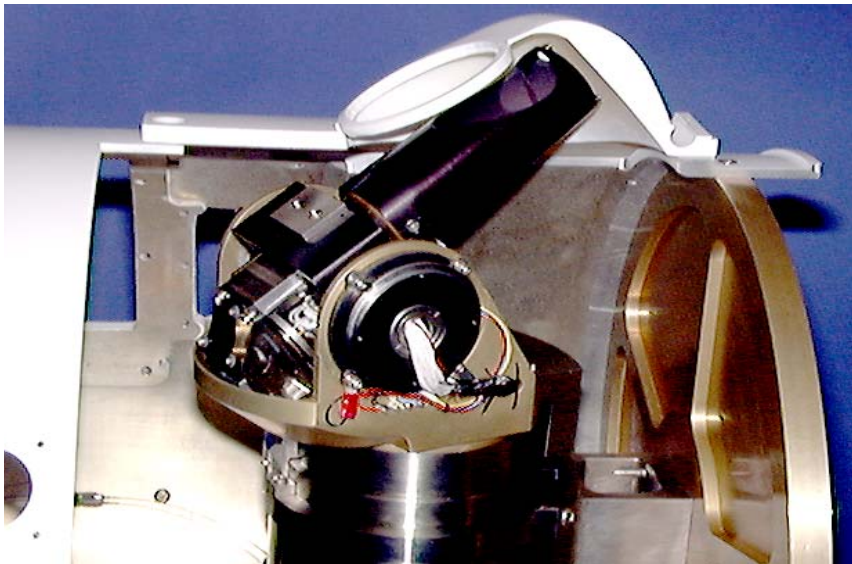
Strain Gauge Measurements Comparable to Predicted Values



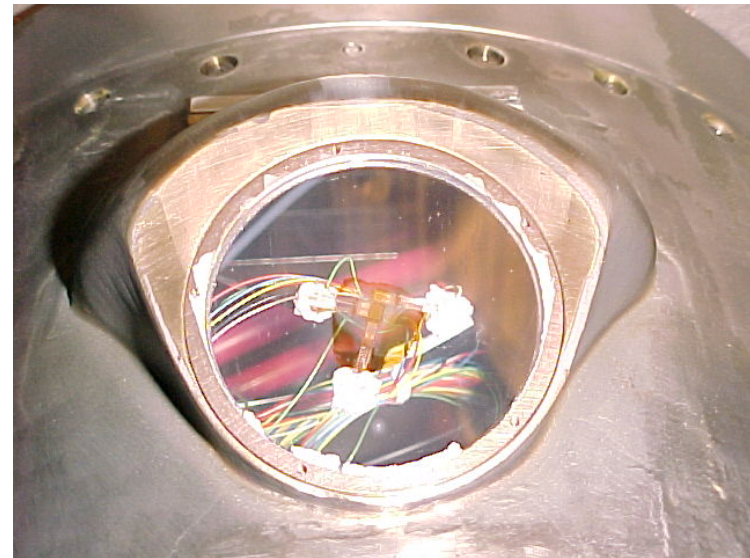
Inner Surface Stress Measurements Similar to Model

Summary - Uncooled Yttria Windows

Alternative, uncooled missile window designs and materials are demonstrating significant tactical and cost savings advantages.



A complete prototype seeker was built and demonstrated to validate mechanical and optical performance.



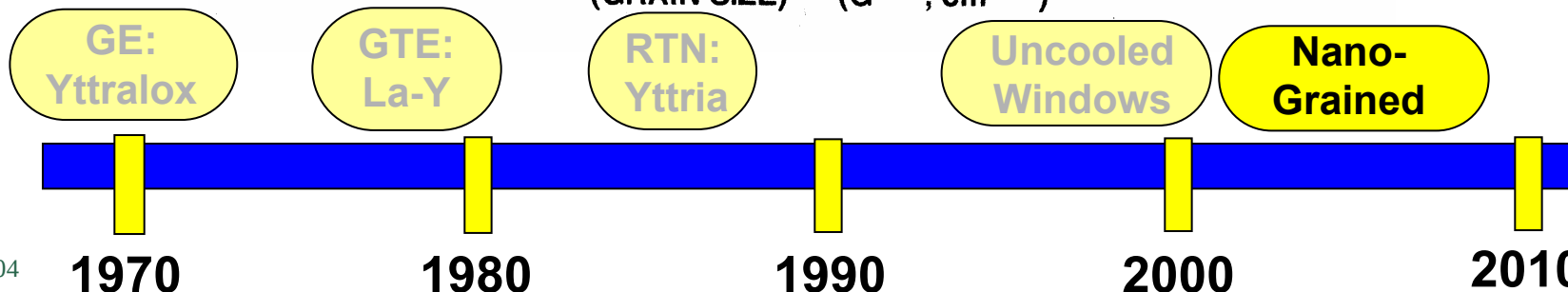
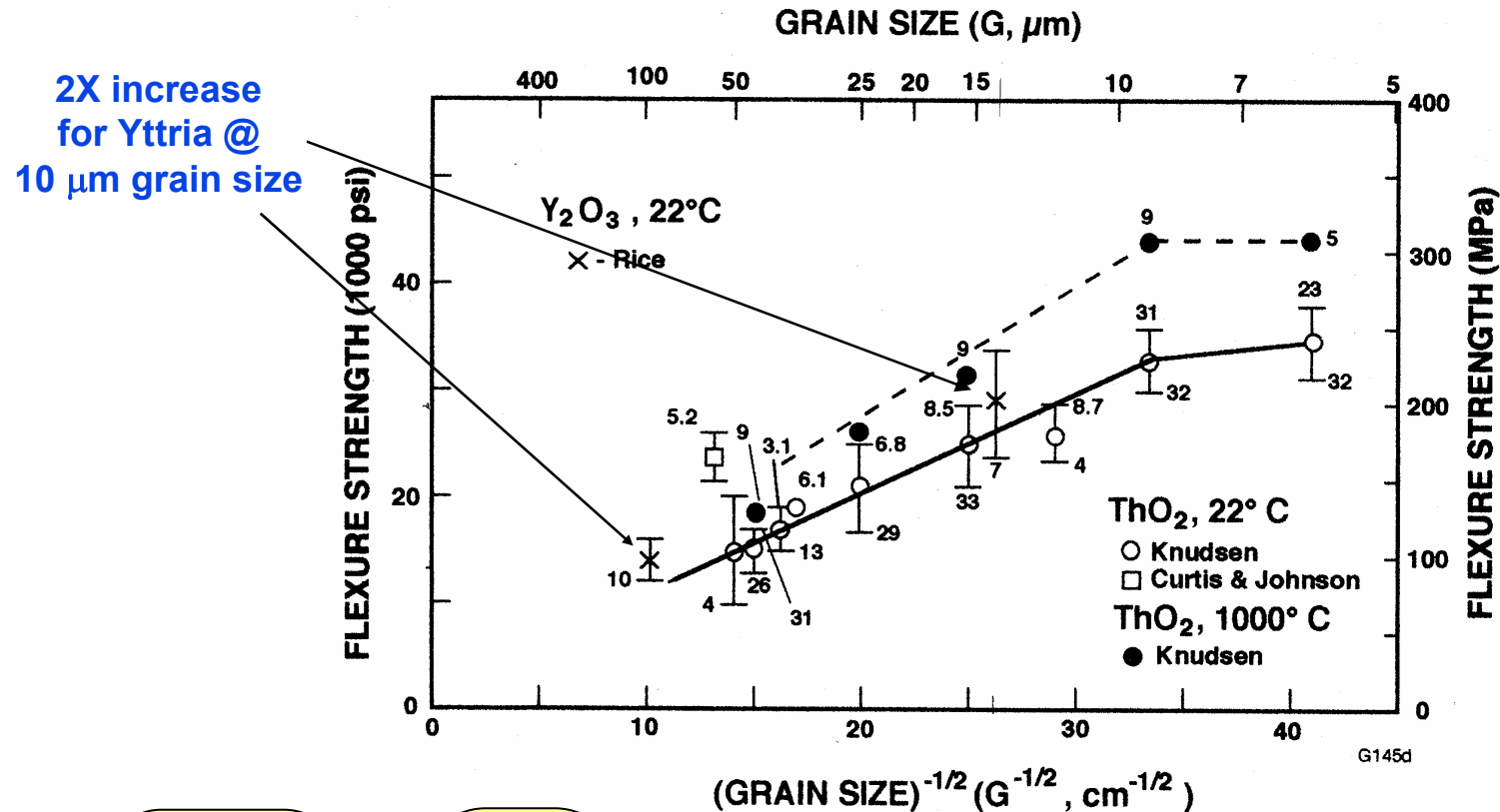
Successful design, fabrication and demonstration at the Navy's APL Wind Tunnel Facility. Reached missile flight conditions with Raytheon flat Yttria material.

**Window was uncooled and survived
7 out of 7 wind tunnel tests.**

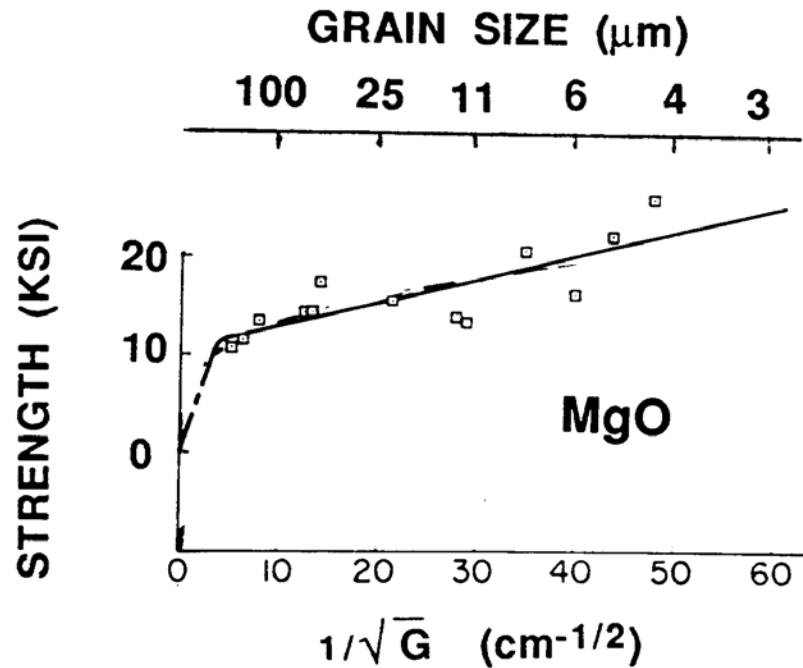
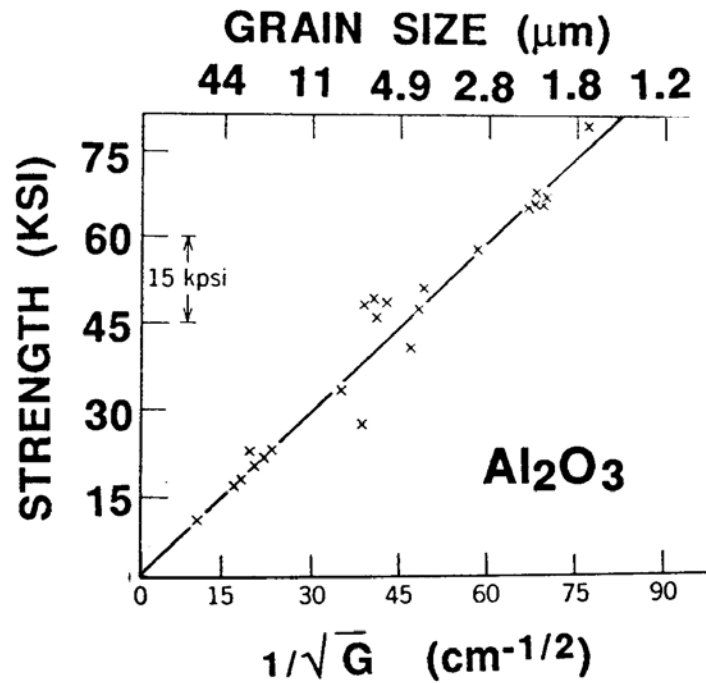
- Flat plate window design meets or exceeds missile performance parameters
- Offset pitch and yaw gimbal minimize window aperture and beam motion
- Yttria window material has optimum combination of properties which enable uncooled side mount design
 - Increases signal to noise by expanding usable waveband
- CFD used to analyze stressing trajectory and predict thermal, structural, and optical performance
- Unconstrained flat window design decreases stress relative to dome designs
 - Surface stresses are compressive
- Early uncover reduces peak stresses, reduces wavefront distortions, maintains acceptable S/N
- Flat window design increases engagement envelope
 - Lower altitude, higher speeds
- Cost savings by eliminating dome cooling system

Nano-grained Yttria

- Smaller grain size in ceramics produce higher strengths, toughness and thermal shock resistance



Dependence of Strength on Grain Size



↓ Grain Size → ↑ Strength

More pronounced effect in non-cubic materials (like alumina)

OVERALL OBJECTIVE:

- **Develop 2X stronger yttria by substantially reducing grain size**

APPROACH

- **Use commercially available nano-powders**
- **Characterize nano-powders:**
 - Purity
 - Particle Size
- **Process to 100% density**
- **Characterize optical and mechanical properties**

Candidate Nanopowders:

- Nano-1: Combustion flame process; 0.15 g/cc bulk density
 - Visibly contaminated with fibers and black “specks”
- Nano-2: Chemical Vapor Condensation (CVC); 0.13 g/cc bulk density
- Nano-3: Precipitation/calcination process; very dense
 - Highly agglomerated particles of sintered nano-crystallites

Previous Nanopowders: Elemental Analysis (GDMS)

Manufacturer	Conv-1	Conv-2	Purity	Nano-1		Nano-2	Nano-3	
Lot			Goals	Lot 1	Lot 2	Lot 1	Lot 1	Lot 2
Element								
B	2.8	4.7	< 5	17	40	11	3.8	7.5
Na	7.9	7.9	< 20	120	320	16	27	33
Mg	0.31	0.21	< 10	25	190	12	3.9	1.6
Al	0.26	3.7	< 100	480	1100	28	660	17
Si	6.9	38	< 20	580	450	280	61	43
P	0.68	< 0.1	< 10	9.4	130	4.5	4.9	1.4
S	3.1	3.7	< 10	310	470	1 wt %*	130	49
Cl	91	13	< 100	7900	8000	130	4600	7300
K	< 1	< 1	< 1	13	24	< 1	< 1	< 2
Ca	< 0.1	0.29	< 1	< 120	< 150	< 8	13	7.1
Ti	< 0.1	0.2	< 10	6.1	5.2	2.2	24	1.2
Cr	0.12	0.09	< 1	0.28	0.36	0.28	0.75	0.12
Mn	< 0.1	< 0.1	< 1	0.79	0.9	0.47	0.35	0.24
Fe	0.33	0.39	< 10	36	31	2.7	3.1	5.4
Co	< 0.05	< 0.05	< 5	2.5	1.5	0.31	< 0.05	< 0.06
Ni	0.14	0.17	< 5	0.94	0.46	0.94	5.9	0.87
Cu	0.17	< 0.1	< 10	6.3	5.5	3.5	2.4	0.79
Zn	< 0.1	< 0.1	< 10	50	27	3.7	7200	390
Zr	< 0.1	0.24	< 50	210	43	< 0.01	1.8	5.5
Ba	< 0.1	< 0.1	< 5	3.1	1.5	1	< 0.1	0.24
La	< 0.05	0.024	< 30	< 27	< 16	< 8	< 6	< 9
Ce	< 0.05	0.25	< 10	6900	1100	7	5.8	22

*GDMS Value, Leco analysis indicated 0.1%

- Acceptable purity was not observed from any n-yttria vendor
- All vendors worked to improve their products

Previous Nanopowder Characterization Summary

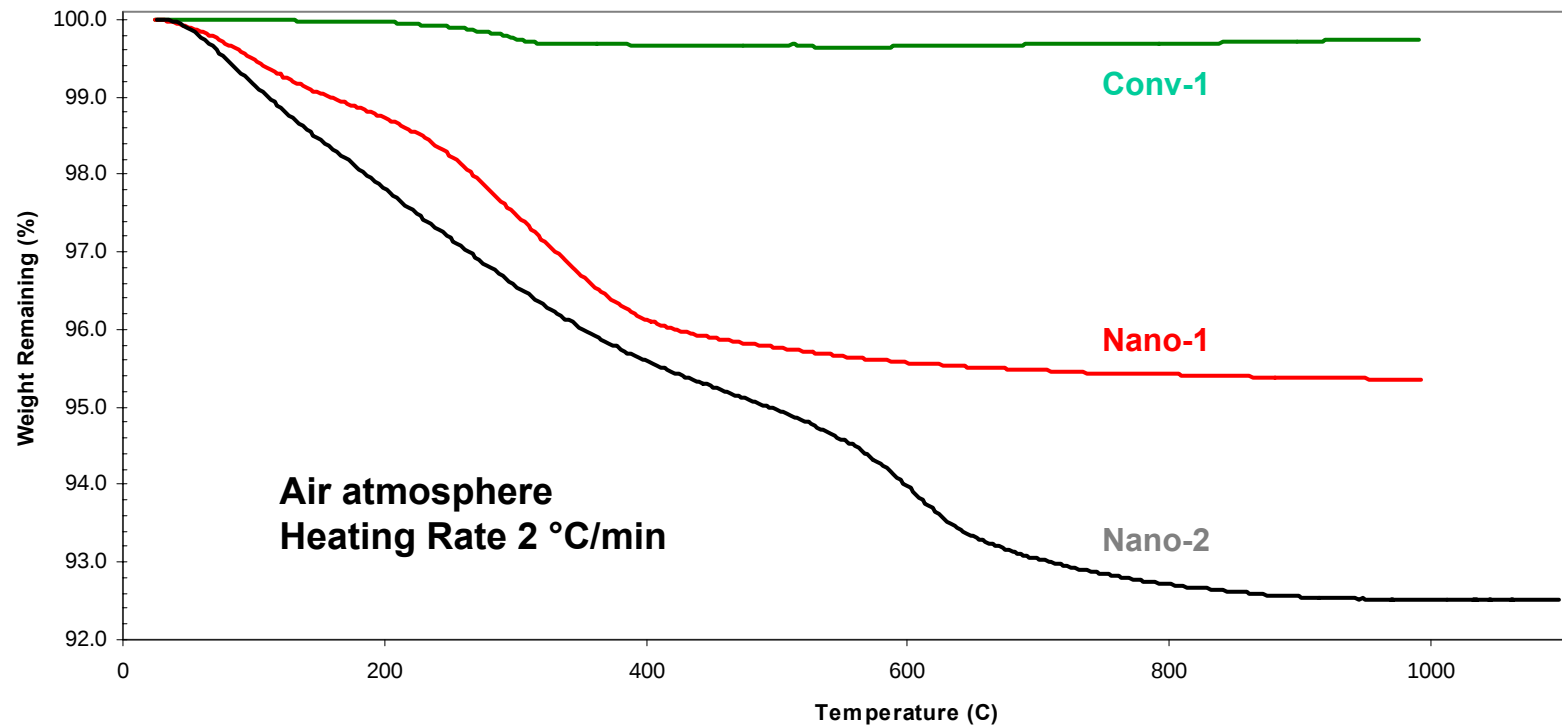
Raytheon
Integrated Defense Systems

Yttria Source	Crystallite Size (nm)	Primary Agglom. Size (nm)	Major Impurities
Conv-1	55	5 um + fines	
Nano-1	40	118	B, Na, Mg, Al, Si (22.5x), P, S, Cl, K, Ca, Fe, Ce
Nano-2	11	130	B, Si (14x), S, Cl
Nano-3	13	140 + coarse	B, Na, S, Si (2.1x), Cl, Ca, Zn, Ce

agglomerates



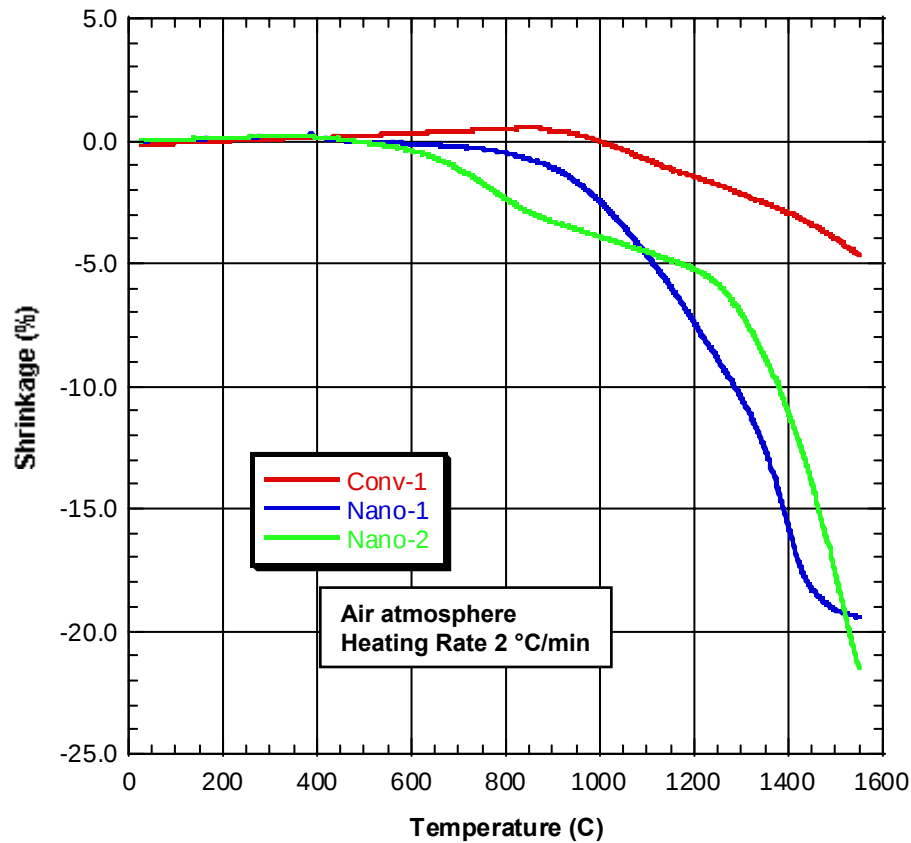
Thermogravimetric Analysis



- **As expected, nano-yttrias contain larger quantities of adsorbed components**
 - Highly susceptible to contamination
 - Optimized process will incorporate cleanroom environment for handling
- **Each powder exhibits characteristic weight loss behavior**
- **Densification parameters must accommodate elimination of adsorbed species**

Densification (1): Dilatometer

Pellets die pressed @ 10 ksi; Isopressed @ 30 ksi



Lower densification onset temperatures for nano-yttria powders

Densification Experiments

- Sinter 1650°C, 4 hrs - in air + HIP 1650 °C, 4 hrs, 29,000 psi (argon)
- Anneal 1400°C, 2 hrs, air

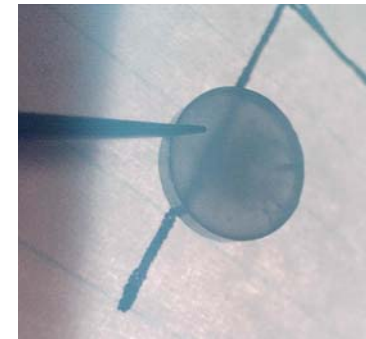
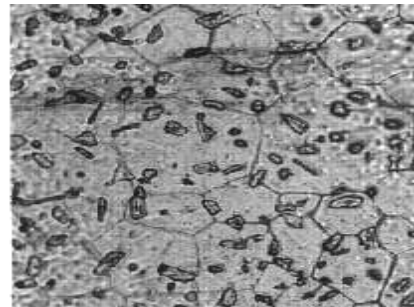
- Nano-1 - 100% dense, but black and opaque. Anneal produced lighter color, but not transparency

(Ce and other impurities)



- Nano-2 - Modest transparency, grain size ~ 60 μm
Anneal produced little change.

(S, Si impurities)



- Nano-3 - 95.3% dense and opaque.
(Incompletely closed porosity prior to HIP)

(Hard agglomerates)



Initial Nano-Grained Yttria

- Initial powders: Not high purity
- Sintering and HIP: Higher than optimum temperatures
- Marginal transparency
- Grain size: 10-50 microns



Nano-grained Yttria Status – as of 2003

- Nano-yttria powders from three vendors (2 batches each) not sufficiently pure to produce transparent ceramics
- Nano-yttria densification begins at substantially lower temperatures than for conventional powders
- Full density and limited transparency were achieved in two nano-yttrias by sinter + HIP at significantly lower temperature
- Glycine nitrate combustion synthesis is a viable method for producing high purity complex nanopowders
- Opportunities for improving all processes

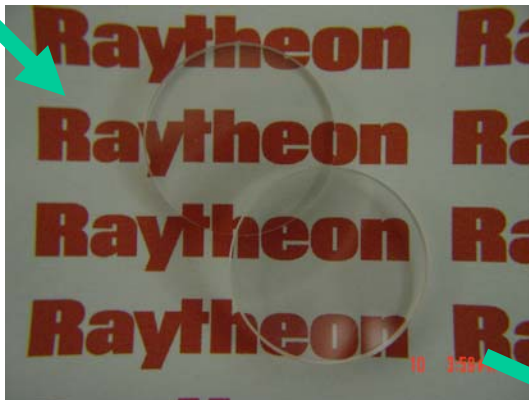
Related Program Ceramic YAG Laser Materials

Raytheon
Integrated Defense Systems

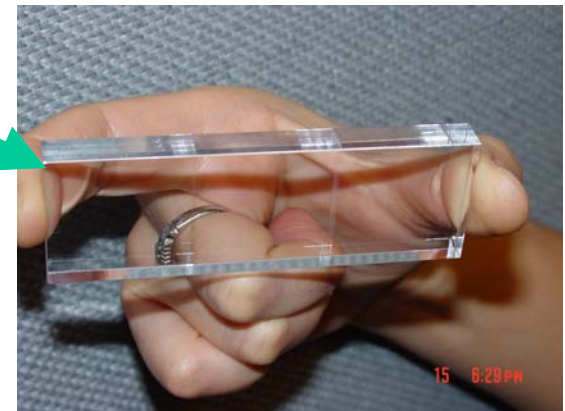


Achieved: Initial
Translucent Samples

Plan:
Improved Materials



Future:
Ceramic Laser Slab

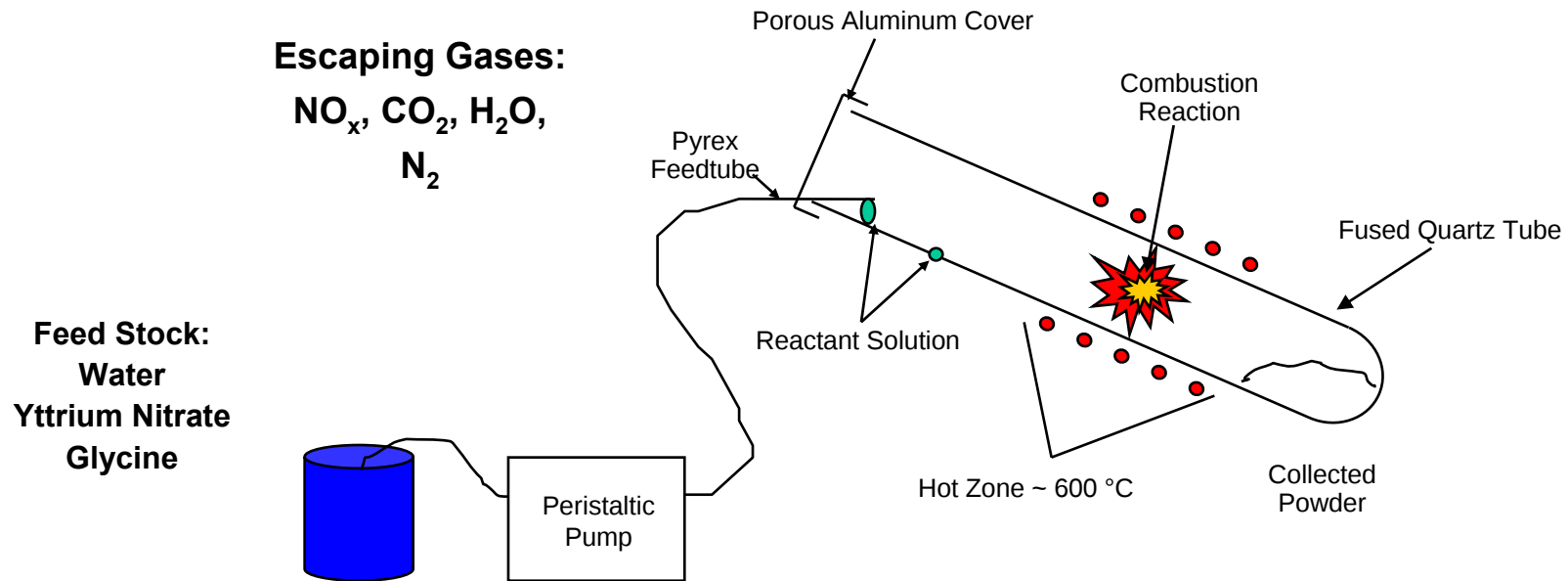


Transparent ceramics work continued during 12 month gap in nano-yttria support

Current Nano-Grained Yttria Activities

- Using higher purity nano-powders from vendors
- Synthesizing nano-yttria powders in house via GNC
- Form green body by wet processing
- Use lowest practical sinter + HIP temperatures
- Goal: High transparency and > 2X strengthening ($\sim 1 \mu\text{m}$ grains)

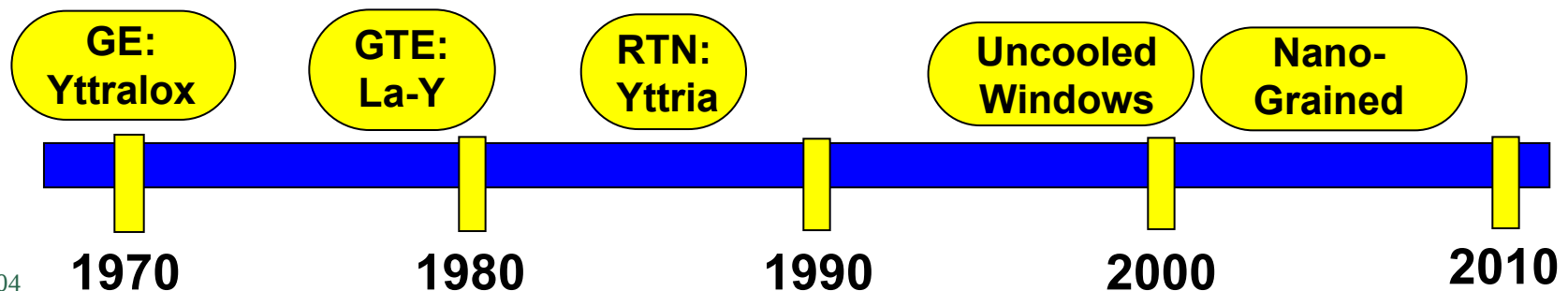
Glycine - Nitrate Combustion Synthesis



- Capable of producing high purity powder
- Minimum measured crystallite size - 9 nm
- Lightly agglomerated
- Highly crystalline
- Demonstrated resistance to grain growth > 45 nm

Summary

- **Yttria has:**
 - Excellent MWIR optical properties
 - Moderate strength ~20 kpsi (~100 micron grains)
- **Uncooled flat yttria windows survived Mach 4+ in wind tunnel**
- **Nano-grained yttria under development**
 - $\geq 2X$ strength increase goal (@ ~1 micron grains)
 - Use high purity nano-powders (PS < 100 nm)
 - Sinter + HIP at lower temperatures to minimize grain growth



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