Optical and Surface Properties of Oxyfluoride Glass

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ABSTRACT

Using conventional materials like fused silica and sapphire for critical window components in a high-power laser system can lead to intolerable thermal distortions and optical path difference (OPD) effects. A new oxyfluoride glass is being developed which has the unique property of possessing a negative thermo-optic coefficient (dn/dT) in the near- and mid-wave infrared. Specifically, the refractive index (n) of oxyfluoride glass decreases as the temperature increases. The distortions caused by thermal expansion of the glass during laser irradiation are partly offset by the negative dn/dT. This paper specifically addresses optical properties and surface finishing of oxyfluoride glass compared to fused silica. Normarski micrographs and surface profiles were measured to inspect the surface quality since smooth surfaces are essential for suppressing surface scattering and absorption. The refractive index and thermo-optic coefficient were measured using null polarimetry near the Brewster angle. Low dn/dT is required for laser windows. Transmittance spectra were measured to deduce the extinction coefficient by comparing with the transmittance calculated from the refractive index and to screen for unwanted absorption from contaminants including hydrocarbon oils, polishing residue, and water or -OH groups. Total integrated scattering was measured for both surface and bulk scattering. All measurements were done on 1.0- and 1.5-inch-diameter witness samples.

Keywords: Oxyfluoride glass, refractive index, thermo-optic coefficient, surface topography, transmittance, scattering.

1. INTRODUCTION

To select optical windows for high power laser systems, low loss and small change of optical and mechanical properties by heating must be considered. Light intensity loss comes from reflection, absorption and scattering. A good window must have a very low extinction coefficient and low surface scattering. A laser passing through a window may warm it up. Thermal expansion and thermal change in refractive index can change the optical path through the window and so forth affect the performance of the optics. To select a good window, many characteristics must be known beforehand. These include transmittance, refractive index, extinction coefficient, thermal expansion, thermal change in refractive index, scattering, surface roughness and texture, hardness, and solubility. One may obtain some of the intrinsic properties from handbooks but not extrinsic properties like surface roughness and scattering.[1-4] In the fabrication of a new optical material for a laser window, the above characteristics need to be measured. This paper reports on measurements of the surface and optical properties of oxyfluoride glass and comparisons between oxyfluoride glass and fused silica. Relationships between different optical properties are outlined in Section 2. Surface characteristics measured using a microscope and a surface profiler are described in Section 3. Measurement and results for the refractive index (n), transmittance, extinction coefficient (k), the temperature rate of n, and the total integrated forward scattering are reported in Section 4. Section 5 summarizes the investigations. Development of oxyfluoride glass is ongoing so values reported here are likely to change as methods of manufacture and polishing are optimized.

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2. OPTICAL PROPERTIES OF A TRANSPARENT WINDOW

The most fundamental optical property is the refractive index n and the extinction coefficient k. The transmittance through a window is subjected to many different losses: the surface reflection loss, the bulk absorption and scattering, and the surface scattering loss. The normal transmittance T_o with only the reflection loss is related to n by

$$T_o = 16\, n^2 / (n+1)^4 . \tag{1}$$

By neglecting the multiple reflections in the sample, the transmittance T_a subjected to bulk absorption and scattering is

$$T_a = T_o \exp(-4\pi k d / \lambda) \tag{2}$$

where λ is the wavelength, and d the thickness of the sample. Extinction coefficient k includes the bulk absorption and scattering. The effect of k on T_o is negligible compared to the exponential term in Eq. (2). By neglecting the multiple reflections and surface scattering that are very small, the extinction coefficient k can be determined from the measured data of transmittance and n as

$$k = \lambda \ln(T_o / T_{measured}) / 4\pi d \quad . \tag{3}$$

Scattering by surface roughness and contaminants will reduce T further. Surface scattering is caused by the roughness and texture of the window surfaces. The transmittance T_s subjected also to the loss by surface scattering is related to T_a by

$$T_s = T_a \exp\left[(-2\,(n-1)^2\,(2\pi\sigma / \lambda)^2\right] , \tag{4}$$

where σ is the RMS roughness of the window surfaces. The total integrated surface forward scattering is

$$TIS = 1 - T_s / T_a = 2\,(n-1)^2\,(2\pi\sigma / \lambda)^2 \quad . \tag{5}$$

The measurement and results of refractive index, extinction coefficient, transmittance, total forward scattering, surface micrographs and surface profiles for fused silica and oxyfluoride glass samples will be described in the following sections.

3. SURFACE CHARACTERIZATION

Several oxyfluoride glass samples fabricated by Infrared Fiber Systems (IFS) in Silver Spring, MD and two fused silica samples were characterized and compared. Refractive index and thermo-optic coefficient were measured for fused silica Sample A fabricated about 15 years ago in the Naval Air Warfare Center's optics shop to dimensions of 3.86-cm diameter by 9.5-mm thick with one side polished to an average RMS roughness of less than 0.3 nm and the other side fine-ground.[5] Accurate transmittance for Sample A could not be measured and is not reported in this paper because the fine-ground surface resulted in significant scatter losses. However, the weak intensities of the optical absorption bands between the wavelengths of 2.7 and 3.3μm indicate that Sample A has low O-H content and is very likely Infrasil-grade material. Transmittance was measured and is reported in section 4 for Infrasil-grade fused silica Sample B supplied by General Optics (Moorpark, CA) having dimensions of 2.54-cm diameter by 6.35-mm thick with both sides polished to an average RMS roughness of less than 0.3 nm. Refractive index was measured for four oxyfluoride glass samples having dimensions of 3.86-cm diameter by 1-cm thick with 1° wedge and both sides polished to a specular finish. The thermo-optic coefficient was measured for oxyfluoride glass Sample 4. When determining refractive index values using the null polarimetry technique, a 1° wedge is needed to separate the back surface reflection from the front surface reflection of the sample. However, it was impossible to obtain accurate transmittance measurements for the oxyfluoride glass samples in their original configurations with 1° wedge. Sample 2 was later ground to a thickness of 4.9 mm with both sides nearly parallel and repolished to an average RMS roughness of about 1.2 nm, after which visible and IR transmittance spectra were measured. Details concerning the surface characterization of these samples are reported in the following paragraphs of this section.

An Olympus differential interference contrast (DIC) or Nomarski microscope was used to inspect the surfaces of samples at magnifications ranging from 50 to 1000x. Nomarski micrographs taken at a magnification of 500x near the center of the sample are shown in Figs. 1 and 2 for fused silica Sample A and oxyfluoride glass Sample 2, respectively. An area with two narrow scratches was photographed to show that the very smooth fused silica surface was in focus in Fig. 1. There were very few scratches on Sample A. Surface profilometry showed that a small number of the scratches on Sample A were on the order of a few hundred nanometers deep and as much as 5 nm wide. In areas where there were no scratches, the surface roughness of Sample A was less than 0.3 nm and had not changed much since it was first measured.[5] Nomarski micrographs showed that the surface roughness of fused silica Sample B was similar to Sample A. A Nomarski micrograph of Sample B was not included here since there were no scratches or other features on Sample B that could be seen at 500x magnification. In contrast to the very smooth surfaces of fused silica Samples A and B, the surface of the oxyfluoride glass sample shown in Fig. 2 has more texture. Although not included in this paper, additional Nomarski micrographs show that there are more scratches on oxyfluoride glass Sample 2 than on fused silica Sample A. However, surface profilometry showed that the scratches on Sample 2 are very shallow compared to the deeper, more widely distributed scratches observed on Sample A.

The surface profiles, RMS roughness and peak-to-valley (PV) roughness were measured using a KLA-Tencor Model P-10 surface profiler equipped with a 2-μm-radius-60°-diamond stylus and a 1-mg loading. Figures 3a and b are the surface profiles of fused silica Sample A for scan lengths of 100 and 1000 μm, respectively. The surface profiles for Sample A were taken in areas where there were no deep scratches. Surface profiles of oxyfluoride glass Sample 2 for scan lengths of 100 and 1000 μm are shown in Figs. 3c and d, respectively. The spatial frequency of the surface roughness in Fig. 3d is on the order of a few microns and is similar to the size of the texturing seen in the Nomarski micrograph of the oxyfluoride glass surface shown in Fig. 2. The average values for RMS and PV roughness for fused silica Samples A and B, and for oxyfluoride glass Sample 2 for scan lengths of 100 and 1000 μm are listed in Table 1. These average values were obtained from profiles taken at three different locations on the sample. The fused silica samples were polished to a much better smoothness than the oxyfluoride glass samples.

Table 1. Measured values of surface roughness.

	Surface Roughness			
	100 μm Scan Length		**1000 μm Scan Length**	
	RMS (nm)	**PV (nm)**	**RMS (nm)**	**PV (nm)**
Fused Silica Sample A	0.25	1.73	0.29	4.21
Fused Silica Sample B	0.24	1.79	0.30	1.87
Oxyfluoride Glass Sample 2	1.03	6.01	1.24	8.66

4. CHARACTERIZATION OF OPTICAL PROPERTIES

4.1 Refractive Index

Null polarimetry was used to measure the spectra of refractive index (n) of transparent samples between 0.4 and 1.6 μm.[6-8] The light source was a tungsten halogen lamp with a grating monochromator. Polarization of specular reflection from a transparent sample was analyzed. The angle of incidence (θ) was chosen to be near the Brewster angle of the material. Both the systematic errors and the random errors of the NAWCWD null polarimeter have been minimized such that the accuracy of the ellipsometric parameter ψ is about 0.003°. The refractive index is given by[7]

$$n = \tan\theta \sqrt{1 - 4\sin^2\theta \tan\psi / (1 + \tan\psi)^2} \quad . \tag{6}$$

The precision of n is .0001 and has been improved by a factor of 4 compared to Ref. [7, 8]. The error of n caused by an uncertainty in θ is $dn/d\theta \approx 0.054/°$. For a precision of $\delta\theta = 0.01°$, the systematic error is $\delta n = 0.00054$.

The spectrum of n for fused silica Sample A is shown in Fig. 4.1a. The + symbols represent the measured values while the solid line is derived from Handbook values.[3,4] Notice that the measured values of n are slightly larger than the Handbook values. By offsetting the measured θ values by an amount of 0.026° smaller than the measured θ values, it is possible to shift the measured n to match perfectly with the Handbook values, as shown by the symbols Δ. This is equivalent to using the Handbook's n to calibrate the error in the measured θ. The measured spectra of the oxyfluoride glass samples are shown in Fig. 4.1b. These spectra were not calibrated against the fused silica standard. The n of oxyfluoride glass is close to that of fused silica, and differences in n values between the oxyfluoride glass samples are small.

4.2 Transmittance Spectra and Extinction Coefficients

Transmittance spectra were measured using a Cary Model 5G UV-Visible-Near-IR spectrometer for 0.2 μm < λ < 3.0 μm and a Bio-Rad FTS 175 Fourier Transform IR spectrometer for 1.6 μm < λ < 26 μm. The measured transmittance spectrum for fused silica Sample B is shown as the black solid line in Fig. 4.2a. Using the tabulated n values from a Handbook,[3] the transmittance T_o subjected only to the reflection loss was calculated from Eq. (1) and plotted as the dotted line in Fig. 4.2a. The measured spectrum agrees with T_o for wavelengths between 0.5 and 2.5 μm. Using the tabulated k in the same reference, the transmittance T_a subjected also to bulk absorption and bulk scattering is plotted as the gray line in Fig. 4.2a. Since k data in the wavelength range from 2.5 to 3.6 μm depends strongly on the method of manufacture and the presence of OH absorption, k values for these wavelengths are not listed in Ref [3]. For wavelengths where k values were missing in the Handbook, the k was assumed to be zero. In other words, the calculated transmittance data for 2.5 μm < λ < 3.6 μm represents intrinsic values rather than actual values for a commercial grade of fused silica like Infrasil. In other regions of the spectrum, the measured transmittance for the Infrasil-grade fused silica agrees fairly well with that calculated from the Handbook values of n and k.

By neglecting multiple reflection and surface scattering, the extinction coefficient k can be obtained from the measured transmittance spectrum and the calculated T_o from Eq. (3). The solid line in Fig. 4.2b represents the k determined from the measured transmittance spectra and the discrete symbols are the Handbook values. The measured k agrees well with the Handbook values. The precision of the measured transmittance spectra is 0.2%; i.e., measured transmittance values from 0.002 to 0.999 are reliable. Using Eq. (3), the reliable range of k values is from 3×10^{-8} to 4×10^{-4}. For k > 0.0004, instrument noise exceeds the transmitted signal. For $k < 3\times10^{-8}$, the absorption is too small to be observable.

The measured transmittance data for oxyfluoride glass Sample 2 is shown as the solid line in Fig. 4.2c and the T_o predicted from n is shown as the dotted line. The k determined from n and T is shown in Fig. 4.2d. We see that oxyfluoride glass is a good window for wavelengths between 1 and 2.8 μm. As Infrared Fiber Systems continues to improve methods of manufacture, the useful wavelength range for this new oxyfluoride glass will increase. For example, by preparing and casting oxyfluoride glass in an inert atmosphere, the intensity of the small OH absorption band near λ = 3.2 μm is expected to be significantly decreased.

4.3 Thermo-Optic Coefficient

The sample holder was constructed out of poly-ether-ether ketone (PEEK), a high-temperature polymer. The insulating holder isolated the sample from the mount and allowed controlled heating of the sample. A thin-film thermocouple was placed between the back of the sample and the copper-disk-heating element. By waiting ten minutes after a given back-surface temperature was reached, thermal equilibrium for the entire sample was achieved. This was verified several times using a thin-film-thermal couple attached to the front surface of the sample. The precision of the temperature display for the thermocouple was ± 1°C. The sample was heated to different temperatures T between room temperature and 140°C, and n was measured at a wavelength of 1.3 μm using the null polarimetry technique described above. The measured n as a function of T for fused silica Sample A and fluoride glass Sample 4 are shown in Fig. 4.3a and 4.3b, respectively. Data in both heating and cooling periods were recorded and were found to be repeatable. Data taken on different days also was repeatable if the sample position was not changed. Data of n versus T were fit to a linear equation of T, and then dn/dT was obtained. The average dn/dT obtained for the fused silica sample is 1.3572×10^{-5} /°C, and for the oxyfluoride glass sample is -1.4277×10^{-5} /°C. The Handbook value of dn/dT was listed as 1.145×10^{-5} /°C for UV-grade fused silica [Table 7.5 of Ref. 2]. Their data was obtained from the difference of n measured at room temperature and

471°C, and dividing by the difference in temperature. The value of dn/dT for the oxyfluoride glass supplied by IFS is in the middle of reported values ranging from -0.8×10^{-5} to -1.7×10^{-5} /°C for other fluoride glasses and crystals.[2]

4.4 Total Integrated Scattering (TIS)

Transmitted TIS measurements[9] for normal incidence were made using a HeNe laser operating at 0.6328, 1.15 and 3.39 μm. Two pyroelectric detectors were utilized: one monitored the reference signal, and the other was mounted on a Coblentz sphere to measure the collected scattered light. The light source was chopped and the two signals were fed to lock-in amplifiers to suppress the ambient noise. The incident beam diameter was about 2 mm. The inner and outer loss cones have half-apex-angles of 1.5° and 70°, respectively. The noise level of the TIS system is 5×10^{-5}. The measured forward TIS values for oxyfluoride glass Sample 2 are listed in Table 2. The measured forward TIS for the oxyfluoride glass is about 2.4×10^{-4}. This loss is smaller than the minimum loss of 0.001 measurable by the FTIR spectrometer. The forward TIS includes both the surface scattering and bulk scattering so it should be smaller than the loss measured by the transmittance data, and larger than the TIS value estimated from the surface roughness. From Table 1, the RMS surface roughness σ for oxyfluoride glass is about 1.24 nm. Plugging this value of σ into Eq. (5), the forward surface TIS at λ = 0.633 μm is 7.6×10^{-5}. So the measured forward TIS is about four times the surface scattering. This extra loss can be attributed to bulk scattering. The observed k of 2×10^{-6} at λ = 0.633 μm in Fig. 4.2d is attributable to the bulk absorption.

Table 2. Transmitted total integrated scatter. For each wavelength, the average and standard deviation of 19 measured values are reported.

	Ave. TIS ± Std. Dev. (x 10^{-4})		
	λ=0.6328 μm	**λ=1.15 μm**	**λ=3.39 μm**
Oxyfluoride Glass Sample 2	2.36 ± 0.65	2.00 ± 0.67	3.32 ± 0.85

5. SUMMARY

This paper compared the optical properties and surface finishing of oxyfluoride glass with fused silica. Since oxyfluoride glass is a new material under active development, the values reported here are likely to improve as methods of manufacture and polishing are optimized. All measurements were done on 1.0- and 1.5-inch-diameter witness samples. The measured Normarski micrographs and surface profiles showed that fused silica samples have much lower surface roughness than the oxyfluoride glass. The refractive index and thermo-optic coefficient were measured using null polarimetry near the Brewster angle. The measured refractive indices of the two materials are on the same order of magnitude. The measured refractive index for fused silica agreed with the Handbook's values. By using the measured n to calculate the transmittance subjected only to reflection loss, the extinction coefficient was determined from the measured FTIR transmittance. The measured k-spectrum for fused silica also agreed with the Handbook's values. The k-spectrum for the oxyfluoride glass showed that it is a good window for wavelengths between 1 and 2.8 μm. The measured dn/dT for fused silica is slightly larger than what is reported in the Handbook. The measured dn/dT for the oxyfluoride glass is negative and is similar to values of dn/dT reported for other fluoride glasses and crystals. The measured total integrated forward scattering, which also includes bulk scattering, is larger than the surface scattering predicted from the measured surface roughness. All measured optical and surface properties are consistent with one another according to the relationships outlined in Section 2.

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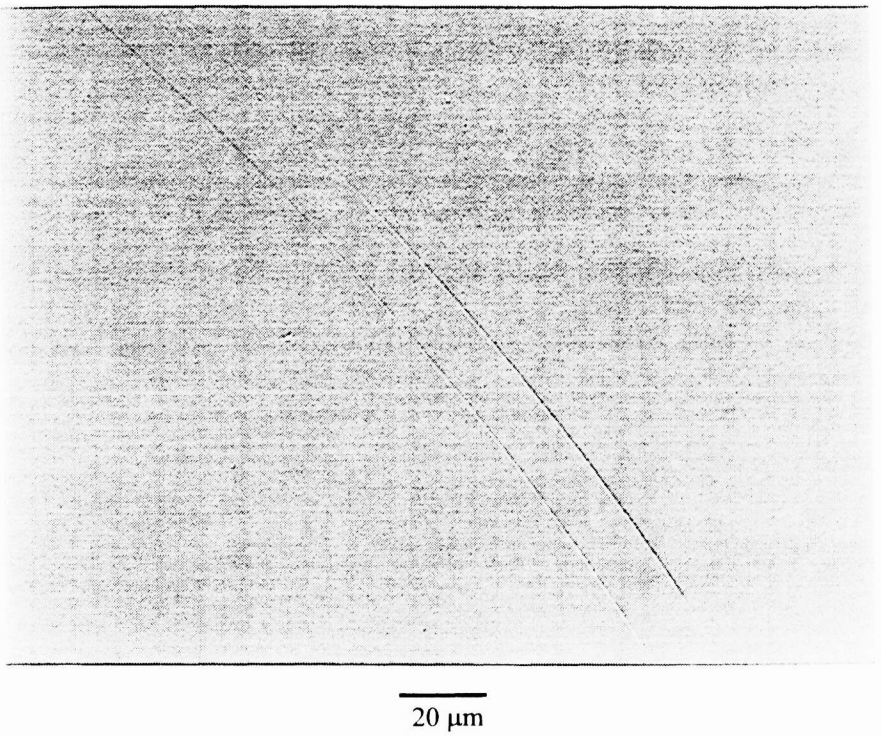

Fig. 1 Nomarski micrograph at 500x magnification of fused silica Sample A.

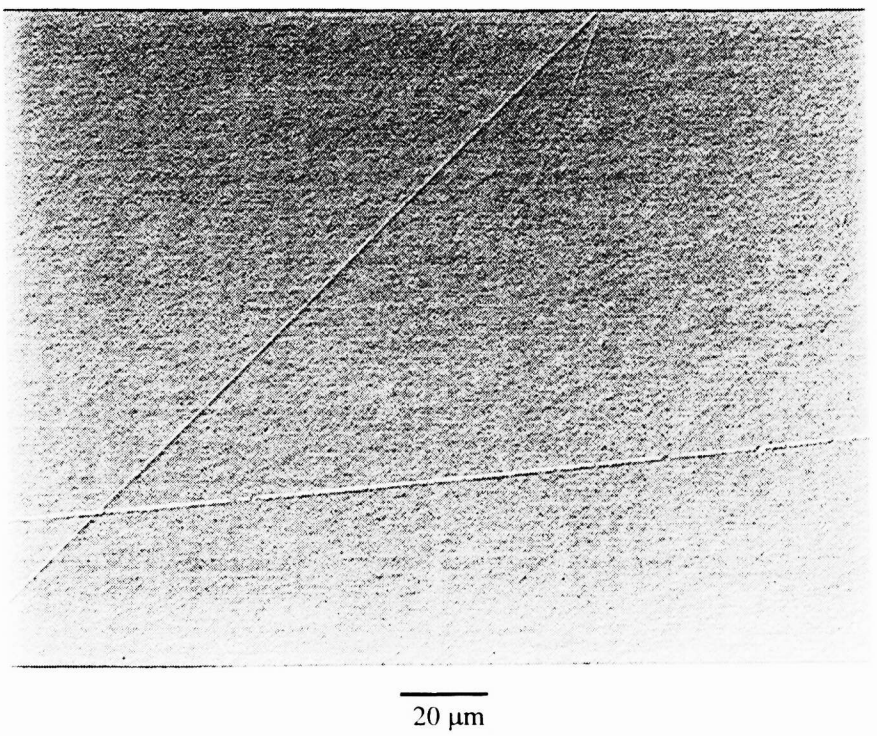

Fig. 2 Nomarski micrograph at 500x magnification of oxyfluoride glass Sample 2.

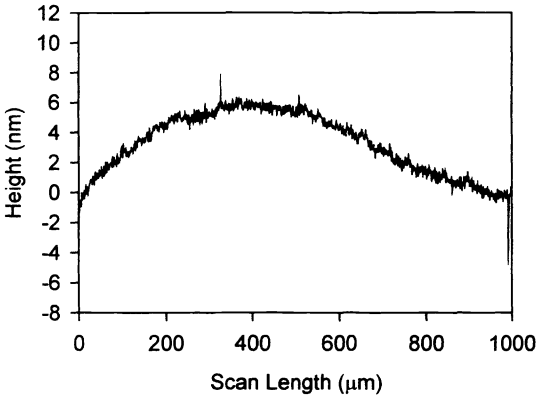

Fig. 3a Surface profile for a 1000-μm scan of fused silica Sample A.

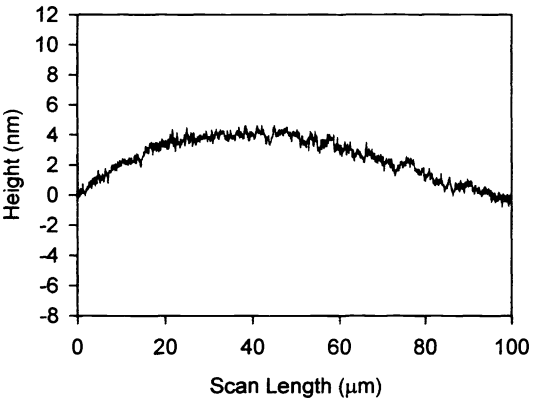

Fig. 3b Surface profile for a 100-μm scan of fused silica Sample A.

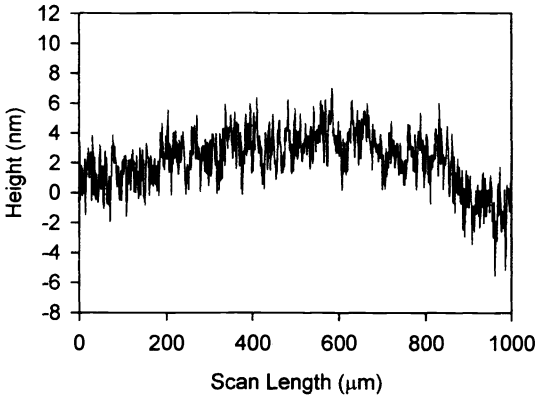

Fig. 3c Surface profile for a 1000-μm scan of oxyfluoride glass Sample 2.

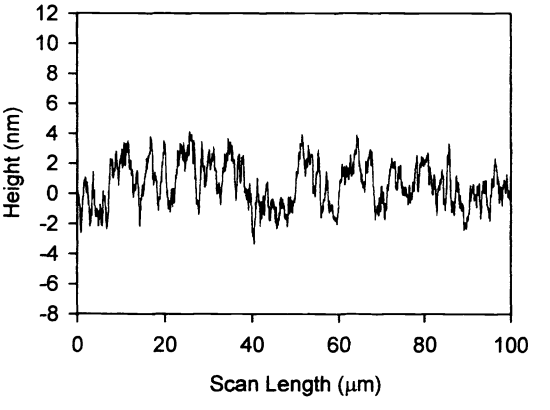

Fig. 3d Surface profile for a 100-μm scan of oxyfluoride glass Sample 2.

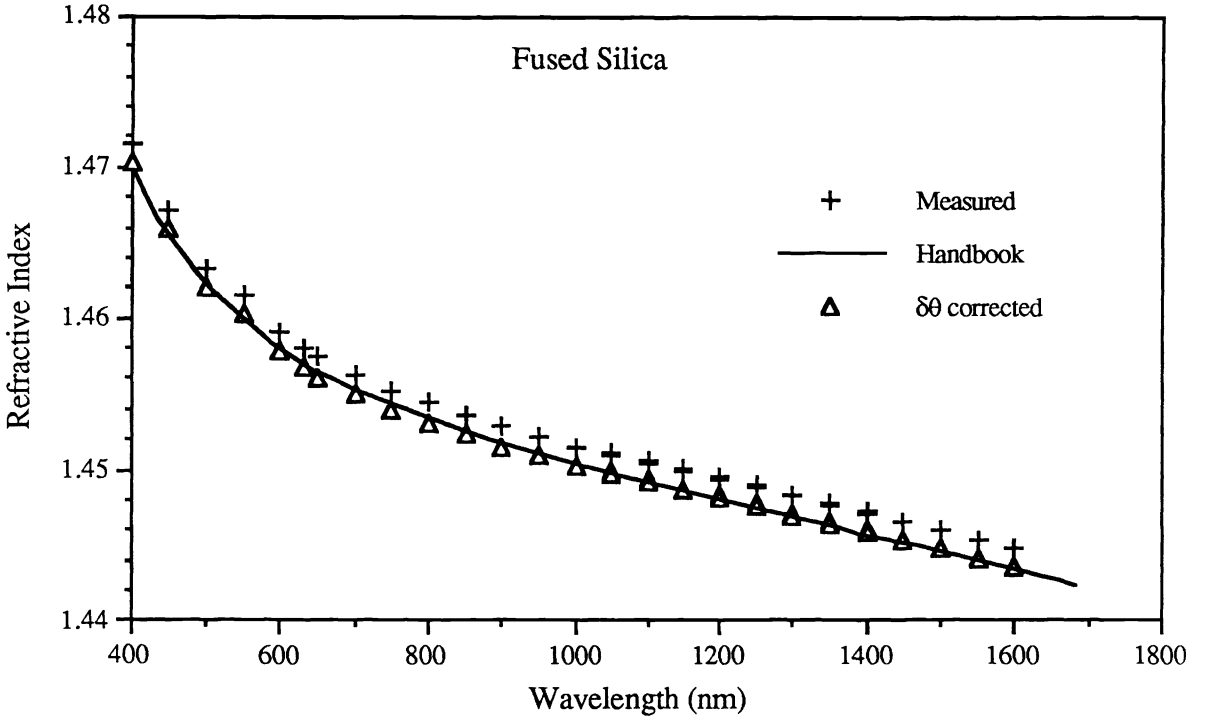

Fig. 4.1a The measured refractive index spectrum (Δ) for a fused silica sample with the correction of incident angle agrees with the spectrum by Handbook (——).

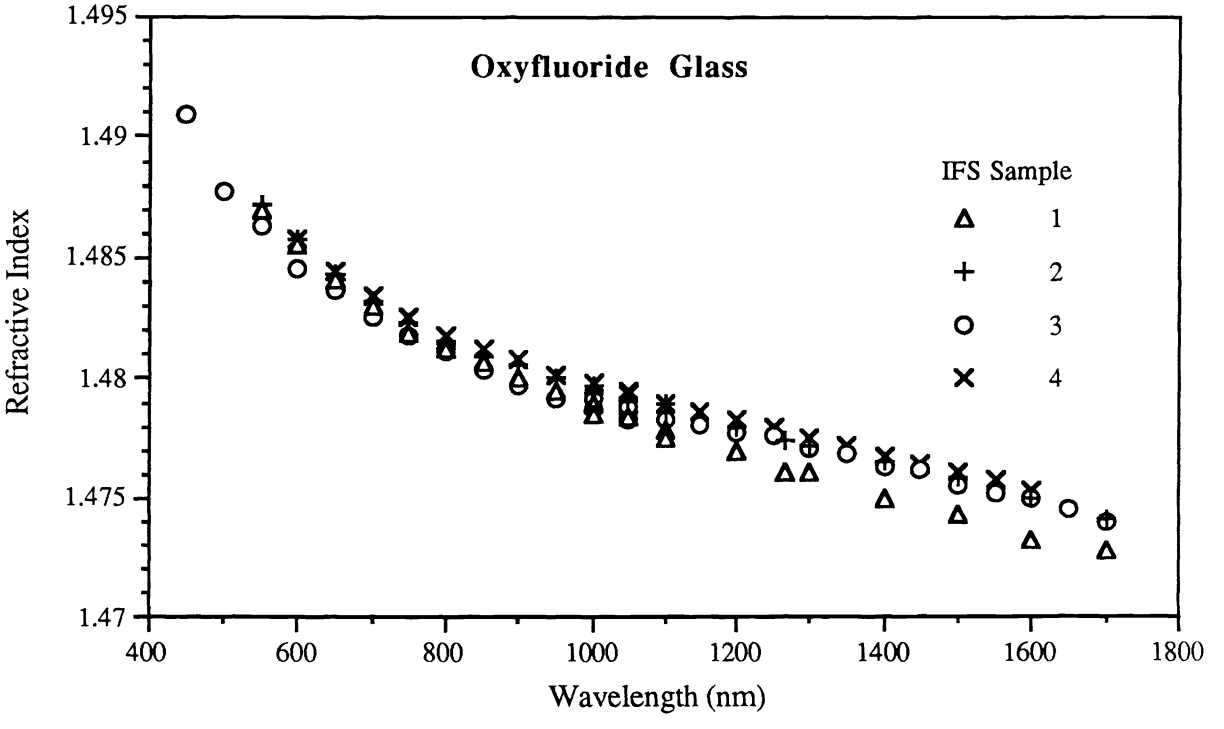

Fig. 4.1b The original measured spectra of refractive index for four oxyfluoride glass samples fabricated by IFS

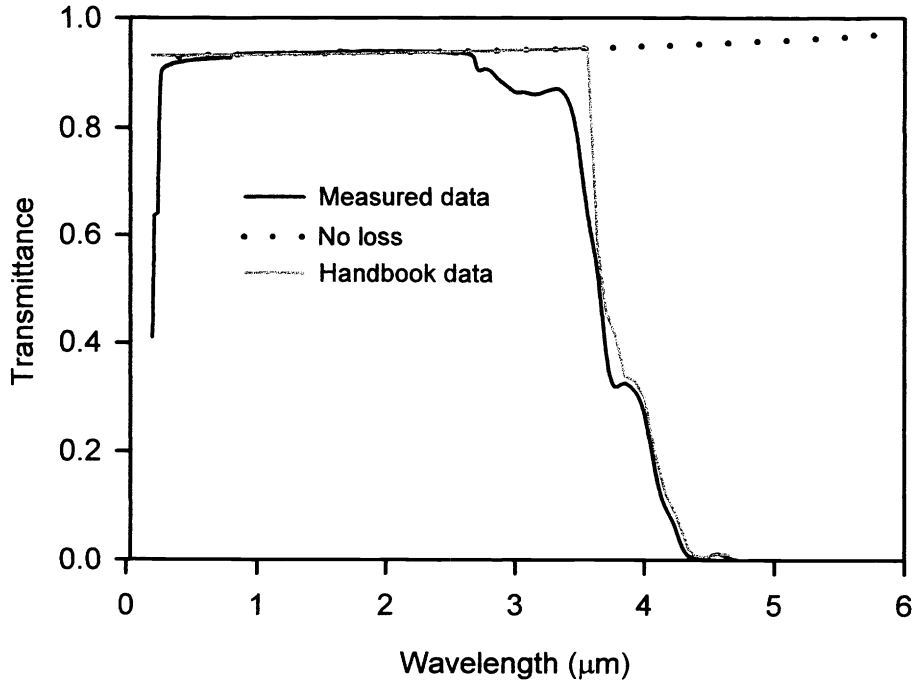

Fig. 4.2a Transmittance of fused silica. The black line is the measured transmittance of 6.35-mm-thick Infrasil-grade fused silica Sample B. The dotted line is the transmittance calculated using Eq. (1) and values of n for fused silica from Ref [3]. The gray line is the transmittance calculated using Eq. (2) and values of n and k for fused silica from Ref [3].

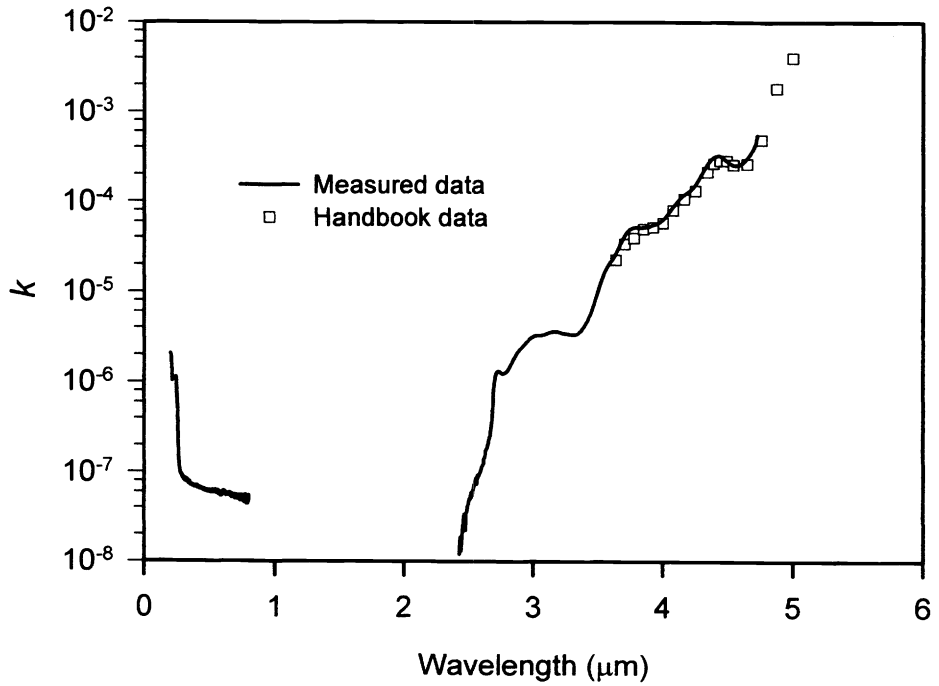

Fig. 4.2b Values of k for fused silica. The solid black line was calculated from the measured transmittance spectrum of 6.35-mm-thick Infrasil-grade fused silica Sample B shown in Fig. 4.2a. The open squares are Handbook values from Ref [3].

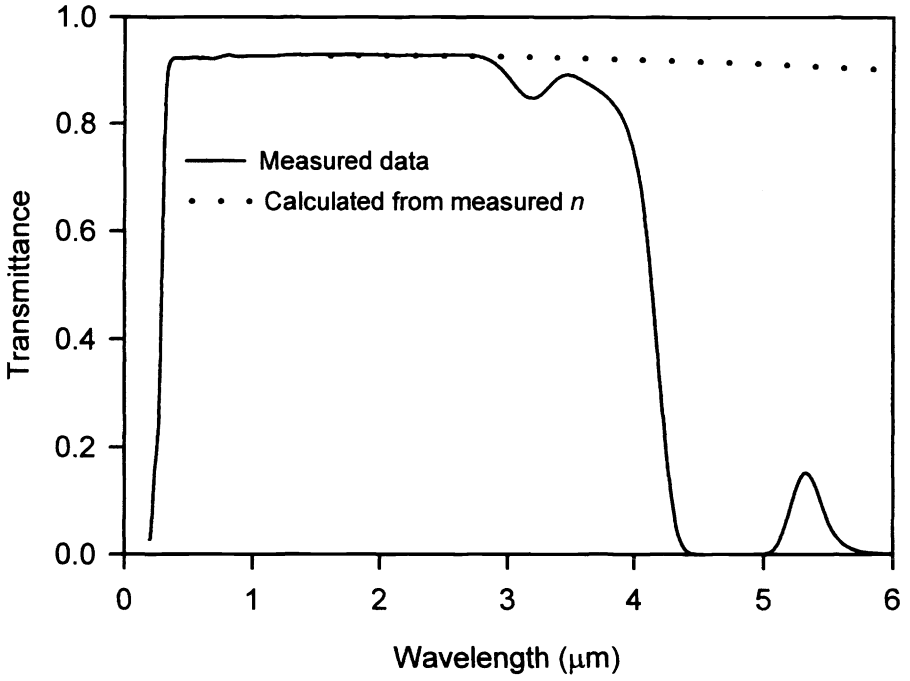

Fig. 4.2c Transmittance of oxyfluoride glass. The solid black line is the measured transmittance of 4.90-mm-thick oxyfluoride glass Sample 2. The dotted line is the transmittance calculated assuming only reflection losses using the average of n determined by null polarimetry for the oxyfluoride glass samples.

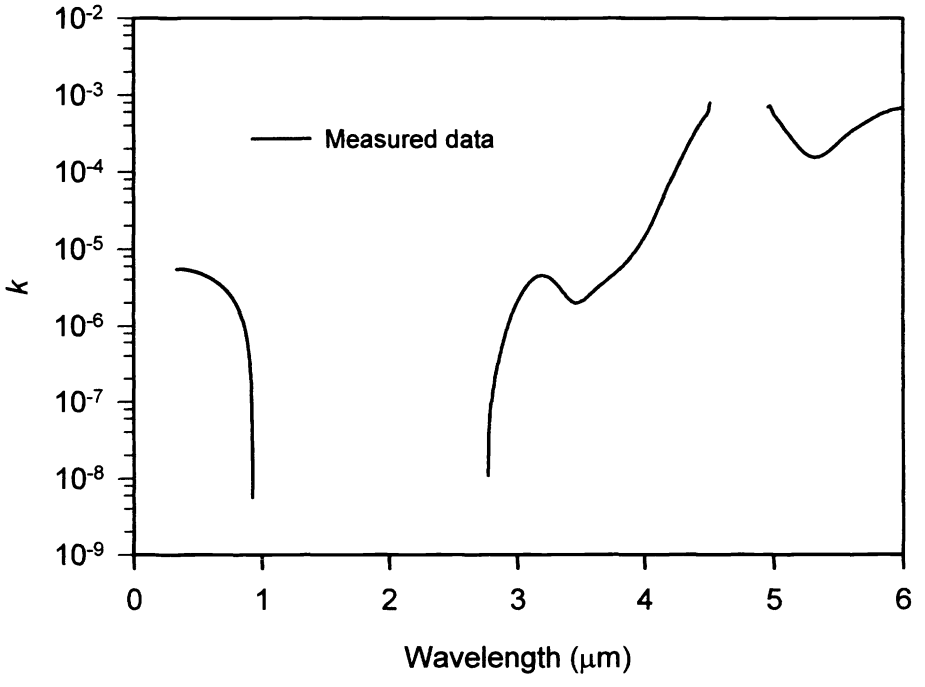

Fig. 4.2d Values of k for oxyfluoride glass. The k values were calculated using n values determined by null polarimetry and the measured transmittance spectrum of oxyfluoride glass Sample 2 shown in Fig. 4.2c.

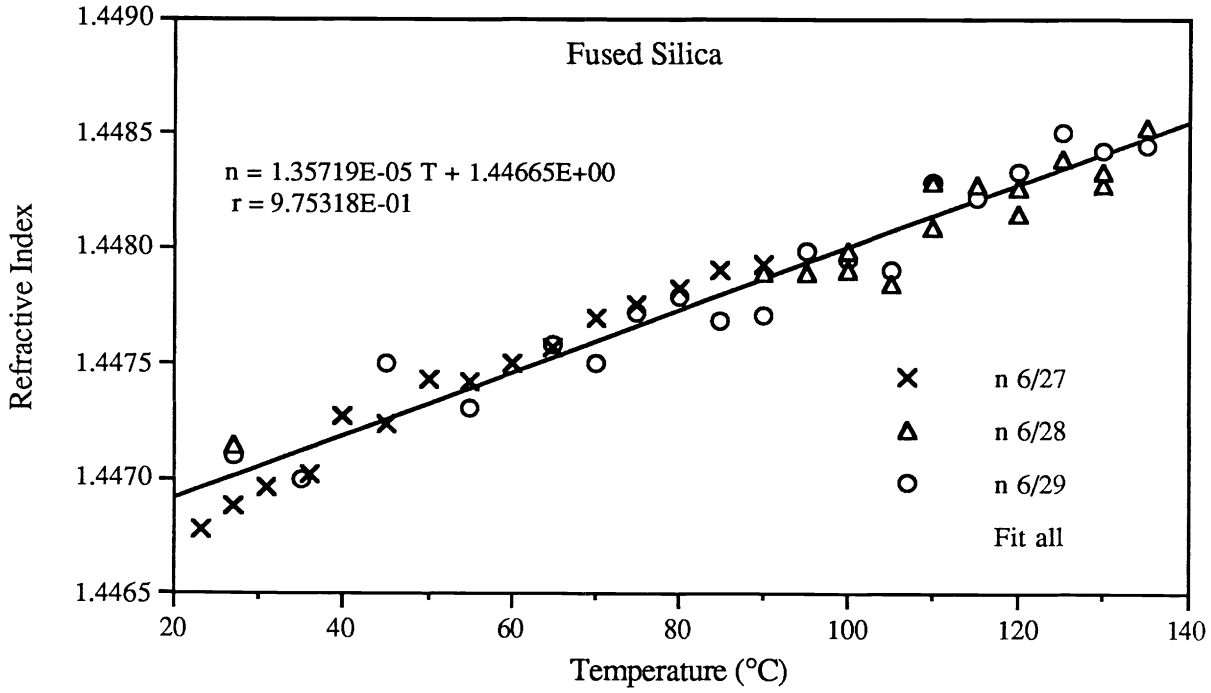

Fig. 4.3a Temperature dependence of refractive index for fused silica Sample A.

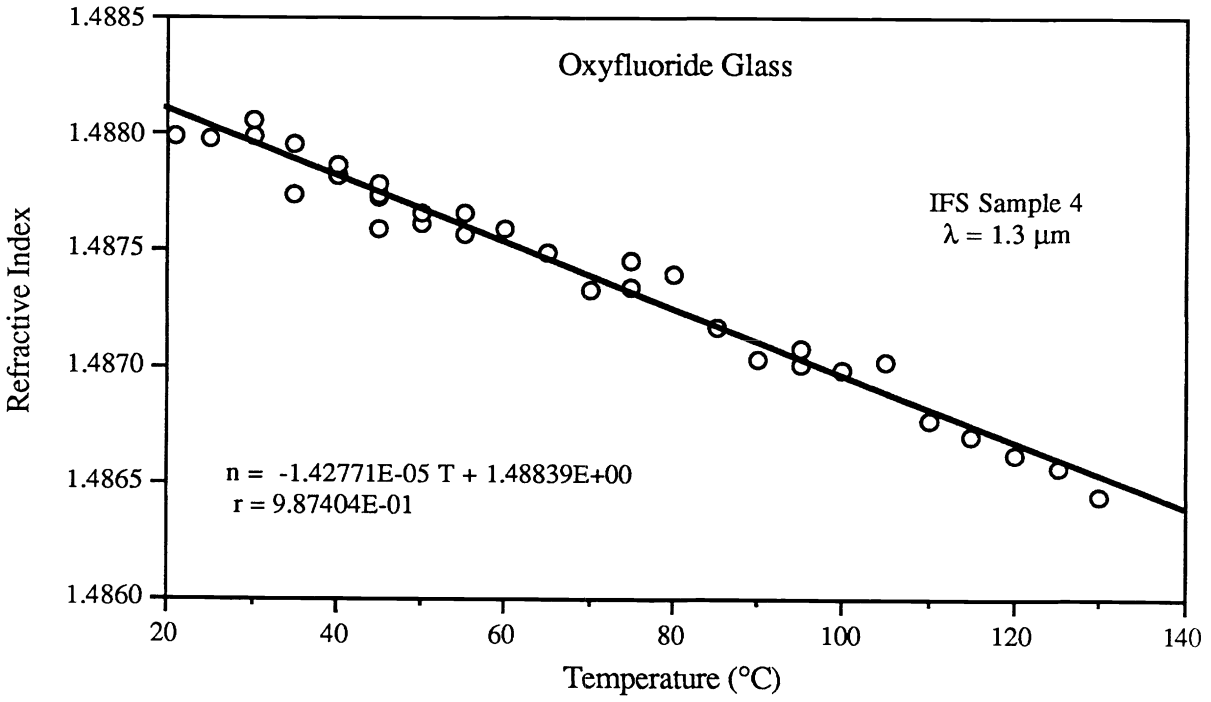

Fig. 4.3b Temperature dependence of refractive index for oxyfluoride glass Sample 4 fabricated by Infrared Fiber System.