

Optical properties of TiO₂–SiO₂ glass over a wide spectral range

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Optical properties of vitreous SiO₂ with 7.4 wt.% TiO₂ are found by dispersion analysis of reflectivity measured in the infrared, visible, and ultraviolet augmented with literature values of vacuum-ultraviolet reflectivity and absorption. The principal infrared absorption associated with the titanium dopant occurs at 950 cm⁻¹ in a deep minimum of the host silica absorption. We attribute this to a perturbation of the silica's absorption at 1076 cm⁻¹ involving oxygen atoms bridging SiO₄ and TiO₄ tetrahedra. Strong ultraviolet absorptions of Ti⁴⁺ occur just below the silica exciton peak between 5.5 and 7.8 eV. We attribute these to charge-transfer transitions at TiO₄ tetrahedra; i.e., bound excitons consisting of a Ti³⁺ ion and a hole shared by four oxygen neighbours.

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1 Introduction Titanium is a common constituent of ceramics and glasses, and silica with a few percent of TiO₂ [1] is used for length standards and astronomical mirror blanks because of its low–even negative–coefficient of thermal expansion [2]. Recently, titania-doped silica played a crucial role in the development of optical fibres [3]. Here we report optical properties from the infrared (IR) to the vacuum ultraviolet (VUV) of titania-silica glass containing 7.4 wt.% TiO₂ measured using synchrotron radiation. At low concentrations, titanium introduces new absorptions at the low-energy side of the principal silica absorptions in both the IR and ultraviolet (UV). We attribute these to perturbed vibrational modes involving Ti–O–Si bonds and to perturbed excitons arising from substitution of Ti⁴⁺ for Si⁴⁺. Applying our results, we show that the frequency for minimum signal distortion in optical fibres depends on the ratio of moments of IR and UV absorptions.

2 Measurements Samples of Corning's ultra-low expansion (ULE) glass [4] ~3.5 mm square and nominally 1.5 mm thick were cut and polished with a wedged back surface to avoid second-surface reflections. Visually, the samples were clear, colourless, with no evidence of either bulk or surface scattering. Their reflectance was measured at room temperature from 18.3 to 32,000 cm⁻¹ with a Bruker IFS 66v/S Fourier-transform spectrometer on beamline U10A at Brookhaven's National Synchrotron Light Source using both synchrotron and black-body sources. These measurements were augmented with literature values of the VUV reflectivity from 2.3 to 12.2 eV reported by Izumitani [5], and Osantowski and Rife's values [6] from 11.8 to 41.3 eV. Philipp's silica data [7] were used as a high-energy extrapolation. The optical constants were calculated by Kramers-Kronig analysis, with direct measurements of the refractive index at the Fraunhofer C, D, and F lines [4] used to anchor the refractive index. Unex-

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pected structure and high reflectance associated with extrinsic absorptions appeared in the near IR from $3,600\text{--}7,300\text{ cm}^{-1}$ ($0.45\text{--}0.9\text{ eV}$). These are likely associated with vibrational modes of OH^- [8], a common impurity in glass [9]. This anomaly was compensated for by interpolating the reflectivity of water-free silica [7] scaled to match the known refractive index [4].

3 Infrared absorption The IR extinction coefficient of ULE glass (free of water) for our composite reflectivity is shown in Fig. 1 together with those for vitreous silica [7] and rutile [10], the usual crystalline form of TiO_2 with octahedrally coordinated titanium. The observed spectrum is remarkably similar to that for vitreous silica, but shows no indication of rutile inclusions. This is consistent with early evidence [11–13] that titanium acts as a glass former at low concentrations, and with measurements of the extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) of Ti [14, 15] and Si [16] K edges. Specifically, for concentrations below $\sim 10\text{ wt}\%$ TiO_2 , titanium substitutes for Si^{4+} as Ti^{4+} in the silica network and “addition of TiO_2 has little effect on the SiO_2 network no significant distortion of the SiO_4 tetrahedron nor change in Si–O–Si bond angle” [16].

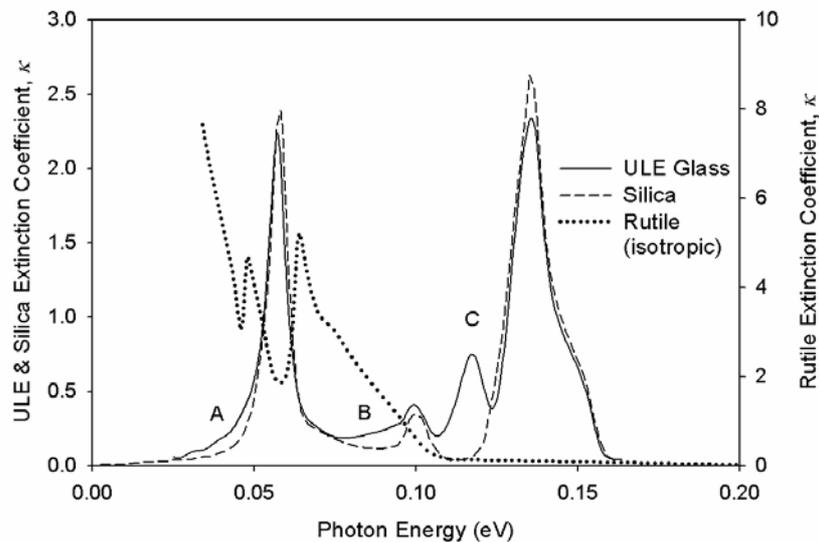


Fig. 1 Infrared absorption of vitreous SiO_2 containing $7.4\text{ wt}\%$ TiO_2 . Spectra for silica and rutile are shown for comparison. The absorptions introduced by titanium are marked as A, B and C.

The principal titanium-associated IR absorption is the prominent band at $\sim 950\text{ cm}^{-1}$ (band C at 0.12 eV) lying just below the host silica's strong 1076 cm^{-1} (0.133 eV) band. This absorption is well documented [13, 17–20]. It has been ascribed to TiO_4 tetrahedra [18], to Ti–O–Si bonds [19], and in this and many other glasses to non-bridging oxygen atoms [17, 21]. Other titanium-associated absorptions occur in broad bands at $240\text{--}400\text{ cm}^{-1}$ (band A between 0.03 and 0.05 eV) and $650\text{--}730\text{ cm}^{-1}$ (band B between 0.08 and 0.09 eV). These lie just below the host-silica absorptions at 450 and 800 cm^{-1} . They have also been reported in differential transmission experiments at $240\text{--}290$, 360 , and $735\text{--}740\text{ cm}^{-1}$ [13, 17].

The introduction by substitutional Ti^{4+} ions of new absorptions just below each of the prominent host silica absorptions suggests that perturbed silica vibrations are involved. The prominent IR-active bands of pure silica are ascribed to TO modes of the SiO_4 network that have substantial motion of the light oxygen ions. These network modes involve vibrations of the bridging oxygen ions of corner-sharing SiO_4 tetrahedra. Focusing on Si–O–Si bonds, Bell and Dean [22], and Kirk [23] attribute the 1076 cm^{-1} silica absorption to a Si–O–Si asymmetric stretching mode; the 800 cm^{-1} absorption to a combination of Si–O–Si in-plane bending and symmetric stretching modes; and the 450 cm^{-1} absorption to Si–O–Si out-of-plane rocking modes. Alternatively, the modes can be described in terms of a linear combination of

symmetry-adapted modes of the linked tetrahedra [24–26]. Wilson, *et al.* [27] projected the results of a network-dynamics calculation on this tetrahedral basis and describe the 1076 cm⁻¹ band as an F₂ stretching vibration, and the 800 cm⁻¹ band as a linear combination of F₂ stretching and bending modes.

Substitution of Ti⁴⁺ for Si⁴⁺ creates four Ti–O–Si bonds, i.e., an isolated TiO₄ tetrahedron with oxygen bridges to four neighbouring SiO₄ tetrahedra. The frequency of modes involving Ti–O–Si bonds (or tetrahedra with these bonds), will be lower because of the greater mass ($m_{\text{Ti}}/m_{\text{Si}} = 1.17$) and the reduction in strength of the Ti–O bond by 0.862 relative to the Si–O bond [28]. This picture explains both the loss in strength of the 1076 cm⁻¹ band in ULE glass relative to silica seen in Fig. 1, and the remarkable strength of the 950 cm⁻¹ band. Specifically, the strength of the 950 cm⁻¹ band is 13–14% of the 1076 cm⁻¹ band in silica while the ratio of Ti to Si atoms in ULE glass is only 6%. The factor-of-two enhancement in strength arises because each *isolated* Ti⁴⁺ ion creates four Ti–O–Si bonds. In contrast, each Si⁴⁺ ion in the silica host is *on average* associated with two Si–O–Si bonds; each of its four bonds is shared by another Si⁴⁺ ion.

4 Ultraviolet absorption The UV extinction coefficient corresponding to our reflectivity composite is compared with that of vitreous silica [7] in Fig. 2. These results are tentative since literature data were pieced together to form a composite: data include our measurements up to ~4.0 eV, measurements by Izumitani [5] (corrected for Na₂O content) from 2.3 to 12.2 eV and data of Osantowski and Rife [6] from 11.8 to 41.3 eV. The most prominent UV features are the strong charge-transfer absorptions, bands D and E,

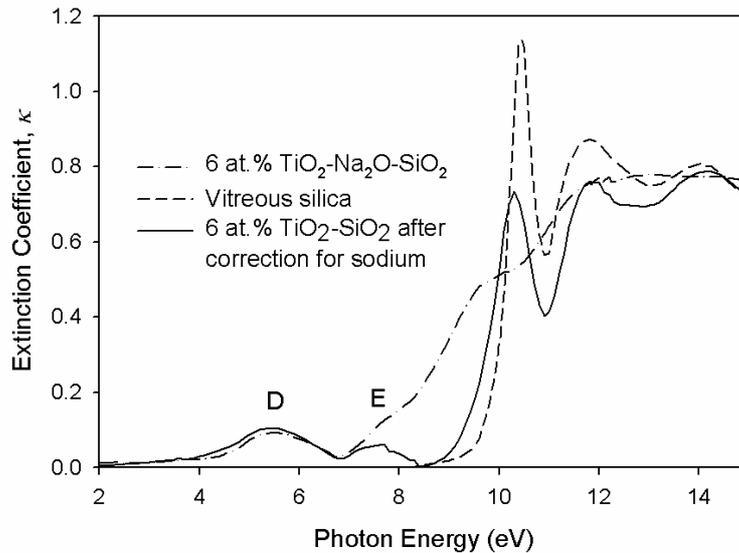


Fig. 2 Ultraviolet absorption of SiO₂ containing 7.4 wt% TiO₂. Titanium-associated bands are marked D and E.

and E, lying below the silica exciton peak that lies at ~10.4 eV [7]. Absorption in the titanium-containing glass rises sharply after ~4.5 eV and reaches a maximum between 5.5 and 6 eV to form the band marked D in Fig. 2. A secondary maximum, the band marked E, lies between 7.4 and 7.8 eV on the low-energy flank of the broadened host-silica exciton. This two-band titanium absorption is consistent with transmission measurements that show a) an absorption edge starting at ~4 eV [13, 29–31] that rises steeply between 5.2 and 6.3 eV; and b) Yano's report [32] of a band peaking at 6.2 eV (with full width at half maximum (FWHM) of 0.8 eV) and a secondary band around 7.6 eV in GE type 219 glass (0.008 wt% TiO₂). We interpret these two absorptions as charge-transfer transitions primarily localized at TiO₄ tetrahedra. Qualitatively, an electron is transferred to the central titanium ion to create a Ti³⁺ leaving a hole shared by the tetrahedral cage of O²⁻ ions, i.e., a localized exciton.

5 Refractive index and group propagation The refractive index, $n(\omega)$, in the transparent region between IR and UV absorptions may be written as a rapidly converging Laurent series by expanding the Kramers-Kronig relations to yield [33]

$$n(\omega) \approx \dots + n_{-2}\omega^{-2} + n_0 + n_2\omega^2 + \dots, \quad (1)$$

where the coefficients are moments of the extinction coefficient, $\kappa(\omega)$, for the IR and UV absorptions:

$$n_{-2} = -\frac{2}{\pi} \int_{\text{IR}} \omega' \kappa(\omega') d\omega', \quad n_0 = 1 + \frac{2}{\pi} \int_{\text{UV}} \frac{1}{\omega'} \kappa(\omega') d\omega' \quad \text{and} \quad n_2 = \frac{2}{\pi} \int_{\text{UV}} \frac{1}{\omega'^3} \kappa(\omega') d\omega'. \quad (2)$$

Group velocity and group index, n_g , for signal propagation may be expressed simply in this formalism:

$$n_g = n(\omega) + \omega \frac{dn}{d\omega} \approx -n_{-2}\omega^{-2} + n_0 + 3n_2\omega^2. \quad (3)$$

Change in signal pulse shape during propagation is minimized when the group velocity is a stationary function of carrier frequency, ω . In the present context, this corresponds to a maximum in group velocity, i.e., a minimum in n_g . Setting $dn_g/d\omega = 0$ yields the carrier frequency for minimum distortion, ω_0 ,

$$\omega_0 = \sqrt[4]{\frac{-n_{-2}}{3n_2}} = \left(\int_{\text{IR}} \omega' \kappa(\omega') d\omega' / 3 \int_{\text{UV}} \frac{1}{\omega'^3} \kappa(\omega') d\omega' \right)^{1/4}. \quad (4)$$

This shows that the optimum carrier frequency depends on two parameters: the first moment of the IR extinction coefficient, and the inverse-third moment of the UV extinction coefficient [34]. Examples for silica and ULE glass are given in Table 1. The important point is that, for a given host material, the parameter that can be varied most easily to achieve a given, ω_0 , is the UV moment, which is determined by the dopant's electronic structure. These results can be further interpreted as showing that the frequency for minimum distortion corresponds to a balance between IR and UV polarization effects.

Table 1 Index coefficients for Eq. (1), and the frequency for minimum pulse distortion.

Material	n_{-2} (eV ²)	n_0	n_2 (eV ⁻²)	ω_0 (eV)
Vitreous Silica	-5.19×10^{-3}	1.47	2.01×10^{-3}	0.962 (1.29 μm)
ULE Glass	-5.30×10^{-3}	1.48	2.57×10^{-3}	0.910 (1.36 μm)

6 Conclusion We measured the optical properties of silica glass containing 7.4 wt% TiO₂ from the far IR to the UV. The spectra confirm that at this concentration Ti⁴⁺ ions substitute for Si⁴⁺ ions to form isolated TiO₄ tetrahedra in the host's glassy network. These titanium units act as colour centres with absorptions in both the IR and UV. In the IR, the principal Ti-associated absorption lies at $\sim 950 \text{ cm}^{-1}$. It is attributed to the asymmetric stretching mode of Ti-O-Si bonds, i.e., to a perturbation of the strong 1076 cm^{-1} absorption of the host's Si-O-Si bonds. In the UV, there are two prominent titanium-associated bands, one between 5.5–6 eV and the other between 7.4–7.8 eV. These are attributed to charge-transfer transitions localized at TiO₄ tetrahedra. They may also be considered as excitons of the host silica perturbed by titanium ions. The effect of dopants such as titanium on light propagation was considered using dispersion theory. This showed that the carrier frequency for minimum distortion of a light pulse is determined by spectral moments of the IR and UV absorptions. Physically the minimum corresponds to a balance between effects of IR and UV polarization. In silicate glasses, the frequency for minimum distortion is determined primarily by the dopant's electronic absorptions in the UV.

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